



AIR RESOURCES BRANCH TECHNOLOGY DEVELOPMENT & APPRAISAL

INTERNAL REPORT NO. ARB-TDA-14-75

FLUOROCHLOROCARBONS AND THE ENVIRONMENT

(A LITERATURE REVIEW)

December 1975

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Ministry
of the
Environment

Ontario

The Honourable
George A. Kerr, Q.C.,
Minister

Everett Biggs,
Deputy Minister

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Ontario Ministry of the
Environment
Air Resources Branch
880 Bay Street, Toronto

December 1975

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1. SUMMARY

Fluorochlorocarbons (FCC's) are a class of compounds containing carbon, chlorine, fluorine and sometimes hydrogen atoms. The most widely used of the FCC's are F-11, F-12 and to a lesser extent F-22. There are no known natural sources of these compounds which are therefore wholly anthropogenic in origin.

FCC's are released to the atmosphere following their use as aerosol propellants (50 percent), refrigeration fluids (28 percent), plastics manufacture (10 percent), and other uses (12 percent). Production of FCC's has grown since 1960 at an average rate of about 8.7 percent per annum leading to an estimated world demand in 1976 of 10^9 kg (10^6 tons).

Production is about equally divided between North America and Europe with Ontario using about one percent of the world total.

The physical and chemical properties of F-11 and F-12 make them uniquely suitable for various uses, however, once released to the atmosphere they are not easily removed by natural processes. These chemicals, which are very low in direct toxicity, are highly insoluble in water, do not take part in atmospheric chemical smog reactions or other reactions in the lower atmosphere (troposphere), and do not adsorb on atmospheric aerosols to any significant extent. Although F-22 is less stable than F-11 or F-12, and can react chemically in the troposphere, its atmospheric lifetime is

still relatively long when compared with lifetimes of most other atmospheric pollutants.

Since 1971 several measurements of "clean" background tropospheric air samples indicate burdens of F-11 and F-12 roughly equal to the total world production of these compounds.

These facts lead Professor Rowland and Dr. Molina (University of California-Irvine) to consider what eventual physical or chemical mechanisms for atmospheric removal (sinks) of F-11 or F-12 could be active. They concluded (June, 1974) that there are no tropospheric sinks of any consequence and that F-11 and F-12 will slowly diffuse upwards above the troposphere and into the stratosphere.

As a result of the higher solar flux at short wavelengths in the stratosphere, FCC's can dissociate there following absorption of solar radiation. The effect of this photodissociation, and ensuing chemical reactions, is to release chlorine atoms to the stratosphere which can then enter a chain reaction reducing the amount of ozone in the stratosphere. It was estimated that a single atom of chlorine at 45 km will destroy, on the average, up to 5000 molecules of ozone every three days. There are no known permanent sinks for chlorine atoms (or chlorine containing species-ClX) in the stratosphere. These ClX species are only removed on diffusion back to the troposphere where they are readily lost by natural weathering processes.

Ozone is a trace constituent in the stratosphere (10 parts per million at 35 km) but it is important since it absorbs

solar radiation in the biologically harmful ultra violet B (UV-B) region (280-320 nm) shielding the surface of the Earth.

The concentrations of ozone in the stratosphere are in a dynamic balance. It is constantly being formed as a result of absorption of solar radiation by oxygen in the upper levels of the stratosphere and ensuing chemical reactions. This production rate is balanced by naturally occurring destructive chain mechanisms involving mainly nitrogen oxides, and to a lesser extent hydrogen oxides.

Rowland and Molina's theory predicts that injection of ClX species to the stratosphere will reduce the amount of ozone in dynamic balance in the stratosphere and thereby increase the intensity of UV-B radiation reaching the surface of the Earth.

The consequences resulting from this increased radiation are difficult to assess. It has been estimated that a one percent net reduction in ozone levels could produce an increase of two percent in the incidence of skin cancers in the U.S. Other possible effects include increased incidence of sun burning, earlier skin aging, possible eye damage, excess production of vitamin D in the skin, increased incidence of cancer among animals, effects on crops and vegetation, and effects on the climate such as rainfall, temperatures and the variability of meteorological parameters.

It has been suggested that some of these effects could be beneficial to the environment. However, the potential for serious adverse effects is large and the present understanding of the problem does not permit quantitative

or qualitative prediction of net changes that could result from a drop in ozone levels in the stratosphere.

The conclusions arrived at by Rowland and Molina are derived from a mathematical model combining both chemical and physical properties of the atmosphere. At least four other independent groups have carried out similar calculations and, despite varying assumptions, agreement between modeling groups is within a factor of two.

Estimates are that a 0.6 to 1.3 percent reduction in ozone in the stratosphere has already taken place as a result of FCC release to the atmosphere. If release is stopped today this depletion would peak by around 1983 at from 1.3 to 3 percent. It could take at least 50 years for ozone levels to return to their 1972 levels. If FCC use and release continues until 1980 then a peak of 1.5 to 4.5 percent reduction in ozone levels would occur by 1987.

An important characteristic to note is that the effects of released FCC's to the atmosphere are predicted to increase for several years after a halt in their use. It could take from 50 to 150 years for the stratosphere to clean itself of these effects.

The ozone levels in the stratosphere vary considerably with time of day, season of year, and latitude. There have also been observed two and eleven year cycles. Against this variable background it is difficult to measure a small, although significant, net change in ozone concentration. A change of five percent extending for, and measured, over a

period of from 5 to 10 years would be required to identify a net change in ozone concentration.

The economic effects of FCC controls are difficult to predict but could be severe. The extent of effects depends on the scope and timing of controls, and the ability of industry to adapt to other compounds as substitutes for FCC's. Secondary effects such as the influence on industries dependent on refrigeration systems would be widely felt.

Since Rowland and Molina's theory was first advanced, numerous government, academic, and industrial research groups have launched research programs to test the theory. These studies have centered around laboratory measurements of relevant reaction rates, development and use of instruments for the measurement of ClX species in the troposphere and stratosphere, efforts to improve mathematical models, and a search for other possible sources of chlorine input to the stratosphere.

During the summer of 1975 the Air Resources Branch of the Ontario Ministry of the Environment initiated a study, under the "Experience '75" program, to sample and analyse ambient air in the Toronto area.

The purposes were to attempt to quantify the FCC input rate to the atmosphere from the City of Toronto, to investigate the suitability of using FCC's as air mass tracers and to establish base levels of FCC's in Ontario against which future work can be compared. Further studies are being planned.

The Air Resources Branch of the Ontario Ministry of the Environment is keeping close contact with the principal investigators in this field. Because of the global nature of this question, it is clear that if any controls decided upon are to be effective, then agreement on an international scale must be reached.

2. Recommendations

In view of the current state of scientific knowledge concerning the possible consequences of continued FCC usage and the nature and magnitude of the problem, it is proposed that the Air Resources Branch of the Ontario Ministry of the Environment carry out the following recommendations:

- 1) Complete the development of a reliable sampling and analytical capability.
- 2) Initiate a program of FCC monitoring in various areas of the province including a detailed study of the Toronto area. The aim of this program would be to establish background levels of FCC's in Ontario under various meteorological conditions against which future work can be compared and to attempt to quantify the rate of FCC release to the atmosphere from a city such as Toronto.
- 3) Due to the nature and magnitude of the problem it is recommended that Ontario not initiate a direct program of stratospheric measurements or research but rather direct help, to the extent possible, towards any federal programs.
- 4) The Air Resources Branch of the Ontario Ministry of the Environment should maintain a continuing review of this rapidly advancing field by maintaining a close contact with the

principal investigators.

- 5) Due to the international scale of the problem, possible controls should originate with the Federal government and, in order to be effective, international agreement should be reached. In any case, current evidence indicates there is very little additional risk in delaying any controlling action for a period of about two years.

3. Introduction

The ubiquitous observation of CFCl_3 (F-11) in the earth's troposphere was first reported by Lovelock^{1,2} in 1971. Within the next three years at least four sets of measurements for F-11^{3,4,5,6} were reported in clean, background tropospheric air samples.

These and other similar compounds are collectively referred to as fluorochlorocarbons (FCC's) and, due to their chemical and physical properties, are attractive for commercial use as aerosol propellants, refrigerant fluids and other uses. Since the 1950's the manufacture and use of FCC's has grown exponentially. There are no known natural sources of these compounds which may therefore be considered wholly anthropogenic in origin.

The measurement of F-11 and F-12 (the most widely used FCC's) in the troposphere in quantities roughly equal to the integrated global production of these compounds prompted research workers to investigate possible atmospheric sinks and the ultimate consequences of the release of FCC's to the atmosphere.

In a comprehensive study, Rowland and Molina⁷ published their theory predicting the only major sink for F-11 and F-12 of significance is stratospheric solar photodissociation with an ensuing injection of chlorine containing photodissociation products (ClX species) to the stratosphere.

Chemical reactions involving ozone, ClX species and other trace constituents can then follow and could lead to a chain reaction resulting in a reduction in the concentration of ozone in the stratosphere. A reduction in ozone concentrations in the stratosphere will result in an increase in

the amount of ultra violet radiation reaching the surface of the earth leading to possible detrimental environmental effects.

Since this ozone depletion theory was advanced many research groups have studied the potential problem. Despite assumptions involved in model calculations, results of several independent groups agree within a factor of two. The theory has not yet been seriously challenged.

4. Structure of the Atmosphere

The atmosphere is usually considered as being divided into horizontal strata or layers of which there are four chief ones using a classification based on temperature as shown in figure one.

The troposphere is the lowest layer extending to an altitude of 15 km over the equator and 10 km over the poles. These levels vary from place to place and season to season being higher in the summer and lower in the winter. Temperature decreases with height at a rate of about 6.5 K per km. Almost all weather processes take place in this layer. Vertical convection keeps the air well mixed.

The upper limit of the troposphere is called the tropopause. This is a narrow and rather uneven transitional zone through which there is little change in temperature.

The stratosphere extends from the tropopause to about 50 km. Temperature increases in this zone from an average of 220 K to 270 K at the top owing to absorption of short-wave radiation by ozone and oxygen. There is very slow vertical mixing in this region of the atmosphere.

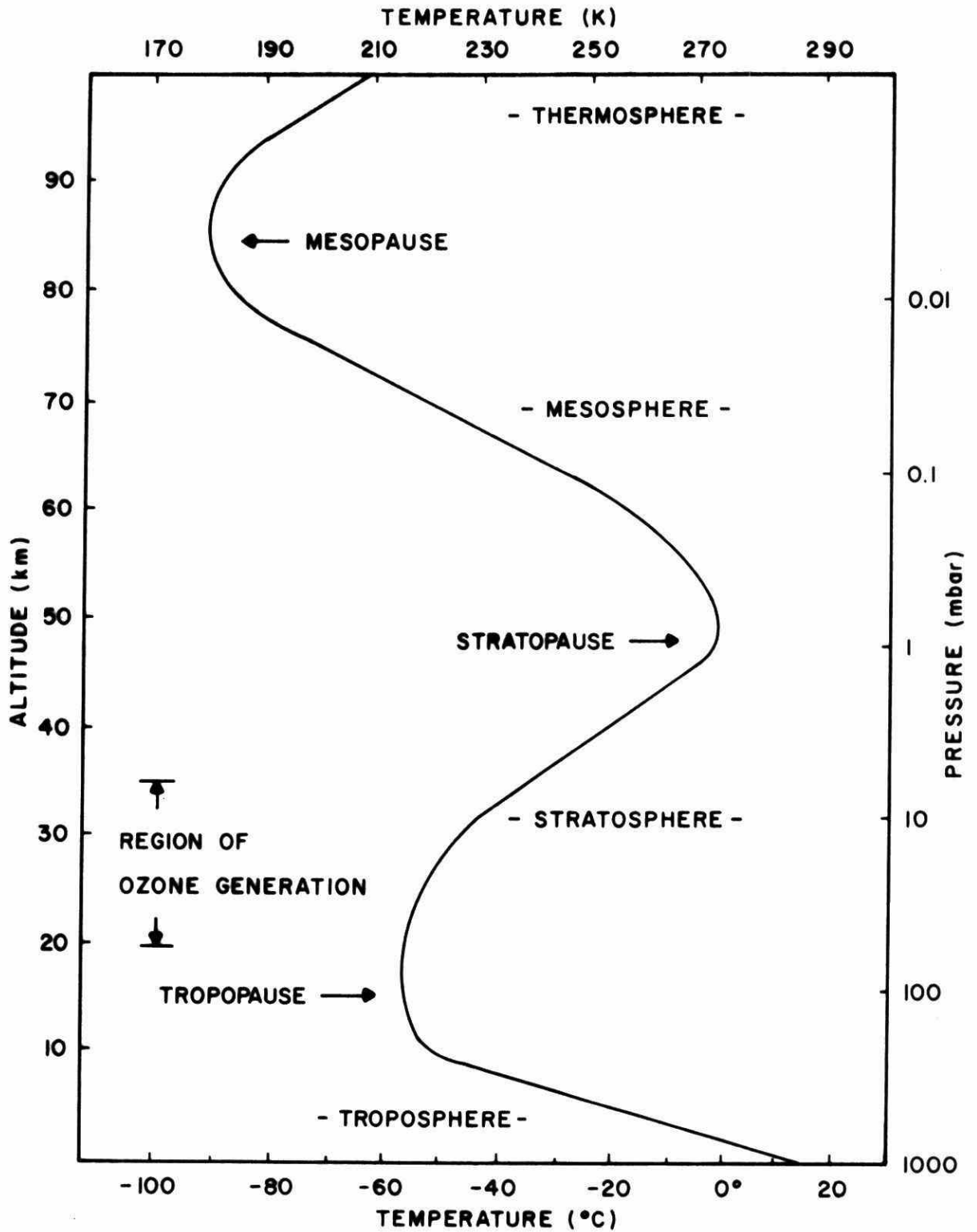


Figure 1: Structure of the Atmosphere

The stratosphere ends at the stratopause which is a transitional region where the temperature is again relatively constant.

The mesosphere extends from 50 to 85 km and is characterized by a temperature decrease with altitude reaching a minimum average of about 174 K (the coldest point in the atmosphere). The mesosphere is terminated at the mesopause which is a transitional region of roughly constant temperature.

The upper layer of the atmosphere is termed the thermosphere. In this region of very low molecular density, intense ultra-violet (UV) radiation dissociates N_2 and O_2 . Temperatures rise to levels in excess of 1000 K.

Nitrogen and oxygen make up 99.02 percent of the atmosphere while nitrogen, oxygen, carbon dioxide, hydrogen and the inert gases make up about 99.995 percent of the atmosphere. Gravitational separation of atmospheric elements is negligible below the thermosphere or about 85 km.

There are, in the atmosphere, many minor constituents which play key roles in determining atmospheric chemistry and determining the solar flux in various wavelength regions reaching the surface of the earth. Of special concern here is the presence of ozone in the stratosphere.

Mixing ratios for ozone in the stratosphere vary from 0.1 to 10×10^{-6} v/v (ppm) with the maximum near 35 km. Ozone in the stratosphere affects the temperature increase with altitude found there and protects the surface of the earth from UV-B radiation (280 to 320 nm wavelength region).

5. Fluorochlorocarbon Development, Usage and Release Patterns to the Atmosphere

a) Historical Development

Fluorochlorocarbons are a class of organic compounds containing one or more carbon atoms, fluorine atoms, and chlorine atoms. Hydrogen may also be present. The principal characteristics of FCC's which make them attractive for commercial use are non-flammability, low toxicity, excellent thermal and chemical stability, high density with a low boiling point, low viscosity and low surface tension.

They were first synthesized in 1928 by General Motors' chemists looking for a non-toxic and non-flammable refrigerant. Since then FCC's have been used in refrigerators and air conditioners as a coolant. It was not until the Second World War that FCC application as an aerosol propellant was first developed for use in an insect spray. Although aerosol insecticides became available to consumers in 1945, they did not flourish in the market place. Heavy steel containers which packaged the highly pressurized product proved overly expensive and inconvenient.

However, during the 1950's two developments occurred which helped to launch the aerosol industry of today. Low-pressure FCC propellants were developed which allowed the use of less expensive and light weight tin and aluminum cans and an inexpensive plastic valve mechanism was invented which could be mass produced.

The result was a remarkable growth in the number of aerosol cans manufactured from 180 million cans in 1954 to more than three billion cans in 1974 in the United States. The latter represents about 50 percent of the total world pro-

duction in 1974.⁹ Canadians used around 160 million cans in 1974. Figure two compares United States and total world production of FCC's from 1958.

b) Nomenclature

FCC's are presently manufactured in over 20 different countries under a variety of trade names¹⁰ such as "Freon" - DuPont trade name, and "Genetron" - Allied Chemical trade name. Table one lists all major producing companies and their product trade names.

The trade name is usually followed by a generally accepted numbering system which may be represented as:

F - abc

where a, b, and c, are digits such that -

- a = the number of carbon atoms less one (third digit from right)
- b = the number of hydrogen atoms plus one (second digit from the right)
- c = the number of fluorine atoms (first digit on the right)

The number of chlorine atoms in the molecule equals that needed for saturation.

For example:

$C_2F_4Cl_2$	is represented by	F - 114
CHF_2Cl	is represented by	F - 22
$CFCl_3$	is represented by	F - 11
CF_2Cl_2	is represented by	F - 12

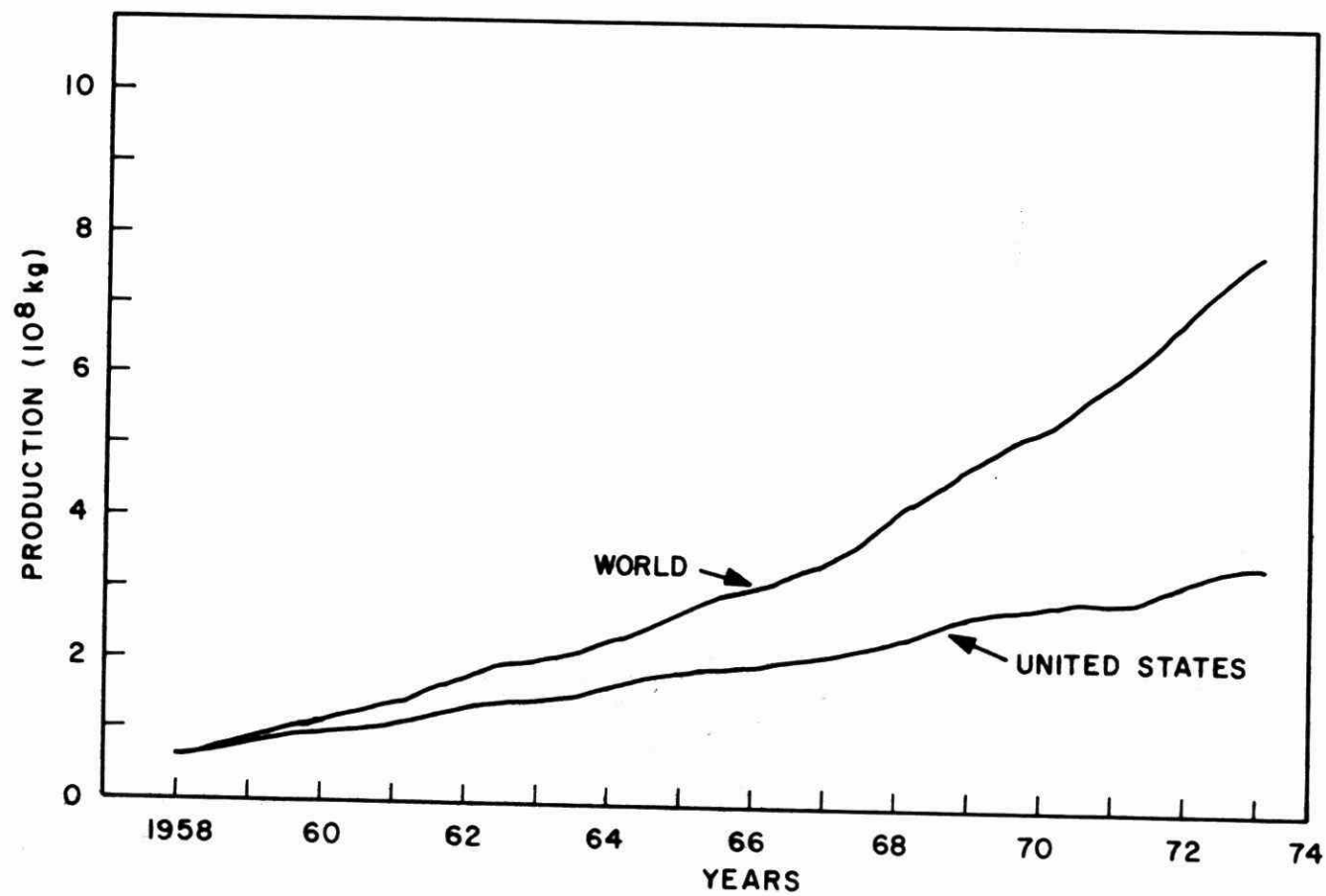


Figure 2: World and U.S. Annual Production of F-11
Plus F-12⁶⁹

TABLE 1. INTERNATIONAL FLUOROCHLOROCARBON PRODUCERS

80

Region/Country	Producing Company	Product Trade Name
<u>North America</u>		
Canada	DuPont of Canada, Ltd.	Freon
	Allied Chemical (Canada) Ltd.	Genetron
Mexico	Halocarburos S.A.	Freon
	Quimobasicos	Genetron
United States	E.I, du Pont de Nemours & Company, Inc.	Freon
	Allied Chemical Corp.	Genetron
	Kaiser Aluminum & Chemical Co.	Kaiser
	Pennwalt Chemical Company	Isotron
	Racon, Inc.	Racon
	Union Carbide Corp.	Ucon
<u>Western Europe</u>		
England	Imperial Chemical Industries, Ltd.	Arcton
	I.S.C. Chemicals, Ltd.	
France	Products Chimiques Pechiney-Ugine-Kuhlman	Forane
	Rhone-Poulenc Industrie	Flugene
Greece	Chemical Industries of Northern Greece*	F-11 & F-12
West Germany	Chemische Fabrik von Heyden AG**	
	Farbwerke Hoechst AG	Frigen
	Kali-Chemi Pharma GmbH	Kaltron
Italy	Montedison S.p.A.	Algofrene
Netherlands	DuPont de Nemours (Nederland) N.V.	Freon
	Akzo Chemie B.V.	FCC
Spain	Ugimica, S.A.	Forane
	Kali-Chemie Iberia S.A.	Kaltron
	Hoeschst Iberica	Frigen

* Startup in late 1975

** All Von Heyden's fluorocarbon production is sold by Hoescht.

TABLE 1. INTERNATIONAL FLUOROCHLOROCARBON PRODUCERS
(Continued-2)

Region/Country	Producing Company	Product Trade Name
<u>South America</u>		
Argentina	Ducilo S.A. Fluoder S.A. I.R.A.S.A.	Freon Algeon Frateon
Brazil	DuPont do Brasil S.A.- Industrias Quimicas Hoechst do Brasil Quimica e Farmaceutica S.A.	Freon Frigen
Venezuela	*** Produven	Forane
<u>Eastern Europe</u>		
Czechoslovakia	Spolek Pro Chemickou a Hutni Vyrobu, Ustinad Labem	Ledon
East Germany	V.E.B. Chemiewerk Nunchritz	Frigedoh
Rumania	(State Authority)	--
U.S.S.R.	(State Authority)	Eskimon
<u>Near Asia and Middle East</u>		
India	Everest Refrigerants, Ltd. Navin Fluorine Industries	Everkalt Mafron
Israel	Makhetsim-Darom Sudbidiary of Koor Chemicals	
<u>Africa</u>		
South Africa	African Explosives & Chemical Industries, Ltd.	Arcton
<u>South East Asia and Pacific</u>		
Australia	Australian Fluorine Chemicals (Pty., Ltd.) Pacific Chemical Industries (Pty. Ltd.)	Isceon Foran Frigen
China	(State Authority)	--

*** Startup in 1976.

TABLE 1. INTERNATIONAL FLUOROCHLOROCARBON PRODUCERS

(continued-3)

Region/Country	Producing Company	Product Trade Name
South East Asia and Pacific (cont'd.)		
Japan	Mitsui Fluorochemicals Co., Ltd Daikin Kogyo Co., Ltd Asahi Glass Co., Ltd. Showa Denko K.K.	Freon Daiflon Asahiflon Flonshowa

c) FCC Production and Usage

The quantities of F-11 and F-12 produced in the United States and in the world have been estimated by R.L. McCarthy¹¹ (see table two). The U.S. production figures are based on U.S. Tariff Commission Reports¹² and probably have an error of less than 5 percent. The figures for world production have an estimated error of 20 percent.

During the period of 1961 to 1971 U.S. manufacture of total FCC's rose by an average annual rate of 8.7 percent with F-12 making up the largest volume. U.S. demand in 1972 was 3.94×10^8 kg and the estimated 1976 demand is 4.5×10^8 kg.¹³

In 1958 virtually all manufacture of FCC's was in the U.S. By 1961 U.S. production of F-11 and F-12 (representing about 85 percent of total FCC production) was about 80 percent of the world total.^{12, 14} This figure dropped to 45 percent by 1973. During the period from 1963 to 1972, when FCC production in the U.S. nearly tripled, the output in the free world outside the U.S. almost quadrupled,¹⁵ an indication of the higher growth rate of aerosol production outside the U.S. Quantities can only be roughly estimated in areas outside the Western world and Japan but they are relatively low.

R.L. McCarthy has estimated, for the production of F-11 in 1971-72, that 44 percent was manufactured in North America,⁷ 48 percent in Europe and 8 percent in Japan.

Usage patterns for FCC's in the U.S. estimated for 1972¹³ are as follows:

Aerosol propellants	50 percent
	(25 percent F-11 and
	25 percent F-12)

TABLE 2. ESTIMATED ANNUAL PRODUCTION OF FLUOROCHLOROCARBONS ^{80 6} (10 kg)

<u>Year</u>	<u>F-11</u>			<u>F-12</u>			<u>Total FCC</u>		
	<u>Canada</u>	<u>U.S.</u>	<u>World</u>	<u>Canada</u>	<u>U.S.</u>	<u>World</u>	<u>Canada</u>	<u>U.S.</u>	<u>World</u>
1974	10.5	138	335	12.0	208	535	25.3	461	1050
1973	8.89	131	317	9.89	195	505	21.8	426	975
1972	7.67	115	298	8.66	186	467	18.9	394	889
1971	6.12	97.5	238	7.98	159	402	16.1	345	767
1970	5.62	100	226	7.21	151	370	14.4	342	719
1969		108	197		167	300			
1968		92.5	165		148	256			
1967		82.6	139		141	225			
1966		77.1	122		130	196			
1965		77.1	116		123	175			
1964		67.1	93.4		103	143			
1963		63.5	83.5		98.4	129			
1962		56.2	71.7		93.9	117			
1961		41.3	51.7		78.5	94.3			
1960		32.7	40.4		75.3	86.6			
1959		27.2	27.2		71.2	71.2			
1958		23.1	23.1		59.4	59.4			

Refrigerants	28 percent (2 percent F-11, 15 percent F-12 and 11 percent F-22)
Plastics	10 percent
Solvents	5 percent
Blowing agents, miscellaneous	7 percent

Canadian production of FCC's for 1974 is estimated as $2.5 \times 10^7 \text{ kg}^{16}$ or 2.8 percent of the world total. Usage patterns are essentially the same as for the U.S (see tables three and four). It is estimated that rates of production and demand are roughly balanced in Canada.¹⁶ Calculated on a population basis, the Ontario demand for FCC's during 1974 was about $9.1 \times 10^6 \text{ kg}$ or one percent of the world total.

It should be noted that only about 50 percent of all aerosol cans manufactured use FCC propellants.¹⁷ These are for such uses as hair sprays, perfumes, colognes, deodorants, air fresheners, pharmaceuticals, frying pan coatings and most insecticides. Cosmetic uses account for more than 90 percent of the total FCC's used in aerosols.

About 45 percent of aerosol cans use hydrocarbon propellants, such as propane and isobutane for shaving lathers, paints, cleansers, furniture polish, rug shampoos, floor waxes, starches, and similar products. The remaining 5 percent use nitrous oxide or carbon dioxide for such items as whipped toppings, windshield de-icers, engine starter fluids, specialty lubricants, and wasp and hornet sprays.

d) Rate of FCC Release to the Atmosphere

The rate of release of FCC's to the atmosphere follow-

TABLE 3. ESTIMATED BREAKDOWN BY USE AND TYPE OF CANADIAN
PRODUCED FLUOROCHLOROCARBONS ⁸⁰ ⁵ (10 kg)

<u>Year</u>	<u>Propellants</u>		<u>Refrigerants</u>			<u>Other</u> [*]	<u>Total</u>
	<u>F-11</u>	<u>F-12</u>	<u>F-11</u>	<u>F-12</u>	<u>F-22</u>		
1974	66.2	77.1	4.5	34.5	**	70.8	253
1973	51.7	60.8	3.6	33.1	13.6	54.9	218
1972	51.3	57.2	3.6	25.4	13.2	38.1	189
1971	41.7	52.6	3.2	23.6	5.9	33.6	161
1970	39.9	51.3	3.2	19.5	7.7	22.2	144

* Includes F-11 and F-12 used as blowing agents, F-113, F-114 and minor amounts of others for solvent and other miscellaneous uses.

** Due to raw material shortage, requirements served by imports of finished product.

TABLE 4. ESTIMATED CANADIAN CONSUMPTION OF FLUOROCHLOROCARBON PROPELLANT BY AEROSOL PRODUCT

<u>Year</u>	<u>TYPE</u> ⁸⁰ (10 ⁵ kg)													
	<u>Insecticides</u>		<u>Paints</u>		<u>Household</u>		<u>Hairspray</u>		<u>Deodorant/ Antiperspirants</u>		<u>Other Aerosols</u>		<u>Total FCC Propellant</u>	
	<u>F-11</u>	<u>F-12</u>	<u>F-11</u>	<u>F-12</u>	<u>F-11</u>	<u>F-12</u>	<u>F-11</u>	<u>F-12</u>	<u>F-11</u>	<u>F-12</u>	<u>F-11</u>	<u>F-12</u>	<u>F-11</u>	<u>F-12</u>
1974	1.27	1.91	0.50	1.13	9.07	13.6	11.3	16.8	25.0	34.5	19.2	9.12	66.2	77.1
1973	1.13	1.68	0.45	1.09	7.71	12.3	10.8	16.2	20.4	27.2	11.2	2.31	51.7	60.8
1972	1.13	1.68	0.41	1.04	6.80	10.4	12.1	18.1	18.1	25.0	12.7	0.95	51.3	57.2
1971	0.95	1.59	0.45	1.09	4.99	9.07	12.9	18.1	15.9	22.0	6.58	0.73	41.7	52.6
1970	0.86	1.50	0.54	1.22	4.54	8.16	12.9	19.3	14.5	20.4	6.58	0.64	39.9	51.3

ing production depends to a large extent on the application. Most studies have assumed immediate release, or release after a period of time, short compared to that of mixing in the lower atmosphere. Attempts have been made to predict patterns of release based on applications¹⁸ (see table five for Canadian figures). Table six presents an estimate of the geographical distribution of release of F-11 to the atmosphere by time period.

Loss during production, transport, and storage can be considered negligible as compared to other sources. With aerosol cans loss to the atmosphere occurs during use. Because of an inventory lag of approximately one year the cumulative quantity released is less than the total quantity produced by an amount equal to the current year's production.

Refrigerant applications can be considered by equating the time at which FCC charge is lost with the life span of the unit. This formula is used for small prefabricated units which are usually factory filled and have an average life of about ten years.¹⁹ Larger units which require recharging on the average every five years can be assumed to suffer a 20 percent loss every five years.

For FCC's used as foaming and blowing agents there is about equal division between open and closed cell applications. Thus, half of this quantity will be released immediately while the other half would remain tied up in the foam matrix for an extended period of time.

Release of FCC's from closed cell foams with fairly short useful lives is small since only about 10 percent of solid waste is incinerated,²⁰ and the more commercially important polyether polyurethanes are resistant to fungal attack.^{21, 22}

Table 5. ESTIMATED ANNUAL RELEASE^{*} TO THE ATMOSPHERE BY USE OF CANADIAN PRODUCED
FLUOROCHLOROCARBONS (10⁸⁰ 5 kg)

<u>Year</u>	<u>Propellants</u>	<u>Refrigerants</u>	<u>Blowing Agents</u>	<u>Others</u>	<u>Total</u>
1974	153	15.4	25.4	3.63	198
1973	120	20.0	23.1	1.81	165
1972	115	16.8	15.4	0.91	148
1971	103	13.2	11.8	0.91	128
1970	95.3	12.3	8.62	0.91	117

*Based on U.S. Estimates of Release:

100% of Propellants
40% of Refrigerants
60% of Blowing Agents
20% of Others

TABLE 6. GEOGRAPHICAL DISTRIBUTION OF RELEASE OF
FLUOROCHLOROCARBON F-11 BY TIME PERIOD
80
(PERCENT)

<u>Period</u>	<u>U.S. and</u> <u>Canada</u>	<u>Western</u> <u>Europe</u>	<u>Japan</u>	<u>Other</u>
1950-1955	46	46	7	1
1955-1960	68	32	0	0
1960-1965	78	22	0	0
1965-1970	93	7	0	0

In solvent applications a recovery system efficiency of 80 percent can be assumed. Inaccuracies here will have little effect on total release figures due to the relatively small quantities used.

In order to project patterns of FCC release, it is necessary to anticipate possible changes in applications. An important example here is the increasing use of FCC's in automobile air conditioning systems. It has been estimated that FCC use for this purpose in the U.S. during 1974 exceeded the²³ total consumer usage for refrigeration systems.

6. Economic Impact of FCC Controls

Although difficult to evaluate, studies to estimate the effects of various controls on the use of FCC's are being carried out by both government and industry.

²⁴
DuPont has stated that during 1975, in the U.S., industry directly dependent on FCC production will contribute more than \$8 billion to the economy. The estimated number of workers involved in these operations exceeds 200,000.

The Domestic and International Business Administration of the U.S. Department of Commerce published an analysis of the effects of FCC controls in July 1975. The effects of a total ban on FCC use in 1978 or 1980 would have almost equal economic severity because the additional two years would be insufficient to develop acceptable substitutes for the FCC's or to complete the redesign of refrigeration equipment.

More than 466,000 employees would be directly affected either by layoffs or curtailed employment in the refrigeration industry alone. Because the time scale would be too short to

develop and test new refrigerants, manufacture and installation of new equipment would terminate with consequent adverse effects on industries dependent on refrigeration.

Industries such as producers of foam for cushioning and insulation materials, fire extinguishing agents, cleaning fluids and solvents, the electronics industry, data processing, and those industries dealing with supply and distribution of food and medicines would be affected.

7. Atmospheric Inventories of FCC's

a) Atmospheric Measurements of FCC's

Since the manufacture and subsequent release of FCC's to the atmosphere has been taking place in large and rapidly growing amounts, and no large tropospheric sinks are recognized, then their presence as a contaminant in "clean" air samples remote from urban areas can be expected.

The first measurements were reported by Lovelock^{1,2,} in 1971 for F-11. Background levels of around 1.0×10^{-11} v/v (10 ppt) were found. Within the next three years at least^{3,4,5,6} four sets of measurements were published for F-11,^{5,6} and two for F-12.

The first measurements by Lovelock were taken on the west coast of Ireland. The lowest levels were found for winds coming from the north-west. Since this air does not pass over any local sources of FCC's, concentrations measured under these conditions were regarded as representative of the northern hemispheric background.

During the voyage of the RRS Shackleton from the United Kingdom to the Antarctic and back (1971-72) Lovelock measured the global distribution of F-11³ finding a variation from 40 to 80 ppt consistent with a largely northern hemispheric source. Except for the variation with latitude the scatter of data was quite small. The mean concentration was reported as (50 ± 7) ppt.

⁵
Su and Goldberg measured F-11 and F-12 in southern California in early 1973. Coastal readings for F-11 varied from 10 to 2,200 ppt and for F-12 from 300 to 8,800 ppt. Although meteorological conditions were not reported the high readings are most likely due to the effect of local FCC sources adding to background levels. Nevertheless, the lowest levels of F-11 are much less than that observed by Lovelock³ and suggest a systematic error between the two sets of measurements. Their desert readings of 97 ppt for F-11 and 700 ppt for F-12 are unexpectedly high for F-12. This mixing ratio for F-12, if applicable to the entire atmosphere of the earth, implies the presence in the atmosphere of 14 megatons which is several times larger than the entire integrated world production of F-12, much of which has been used as a refrigerant and may not yet have been released to the atmosphere.⁷ Since there are no natural sources of F-12 these desert samples cannot represent background levels of F-12 characteristic of a thoroughly mixed troposphere.

⁴
During November and December of 1972 Wilkniss et al measured mixing ratios for F-11 in Pacific air from 15°N to 74°S. A mean of (61 ± 13) ppt³ was reported, showing consistently higher values than Lovelock³ at comparable latitudes, and very little north-south variation.

Reports by Wilkniss et al^{25,26} of more recently collected samples indicate the atmospheric burden of F-11 has increased from late 1972 to early 1974 from (61 ± 13) ppt to (83 ± 6) ppt or 36 percent. Since both sets of results were obtained by the same workers with the same equipment the sets of data may be fairly compared in order to obtain an estimate of the percentage increase of F-11 over the 15-month period. This 1974 value of 83 ppt for F-11 is close to an averaged²⁷ background value of about 90 ppt reported by Lovelock during a voyage from Hamburg to Santo Domingo in October 1973. A²⁸ report by the same author shows background levels of F-11 off the south west coast of Ireland as 68 ppt during June to September 1973.

⁶
Hester et al have collected samples during 1973 in southern California and report levels of 100 ppt for F-12 and 50 ppt for F-11.

²⁹
During May of 1974 Hester et al collected samples by aircraft in New Mexico at altitudes from 6.4 to 18.3 km. These were the first values reported at stratospheric heights.

³⁰
Measurements taken by Lovelock over England in June²⁹ of 1974 at altitudes up to 10 km and by Krey up to 19.2 km are both in agreement with Hester's values.

Many groups are currently involved in attempts to sample for FCC's at high altitudes using balloons, rockets, and aircraft. Lovelock has recently sampled to an altitude of 16 km by jet plane and plans to take still higher altitude samples.

The National Center for Atmospheric Research (NCAR-Boulder, Co.) has begun a series of balloon launchings. Three balloons have been sent to altitudes up to 35 km over the U.S. midwest between September 1973 and June 1975. Results were augmented by a rocket sent to 45 km in 1973. FCC's were found to reach altitudes of at least 40 km at concentrations consistent with predictions using transport and photochemical models.³¹

During June 1975 a series of balloons were launched in Southern Saskatchewan as part of a joint project between the Atmospheric Environment Service of Environment Canada and the U.S. National Oceanic and Atmospheric Administration (NOAA). Samples were obtained at heights of 18 to 22 km. F-11 and F-12 were detected at concentrations and vertical distributions predicted by model calculations.³² The combined NCAR and NOAA results are presented in figure three.

In addition, the U.S. National Aeronautics and Space Administration (NASA) is supporting at least three satellite observations of the atmosphere in support of the broad FCC examination.

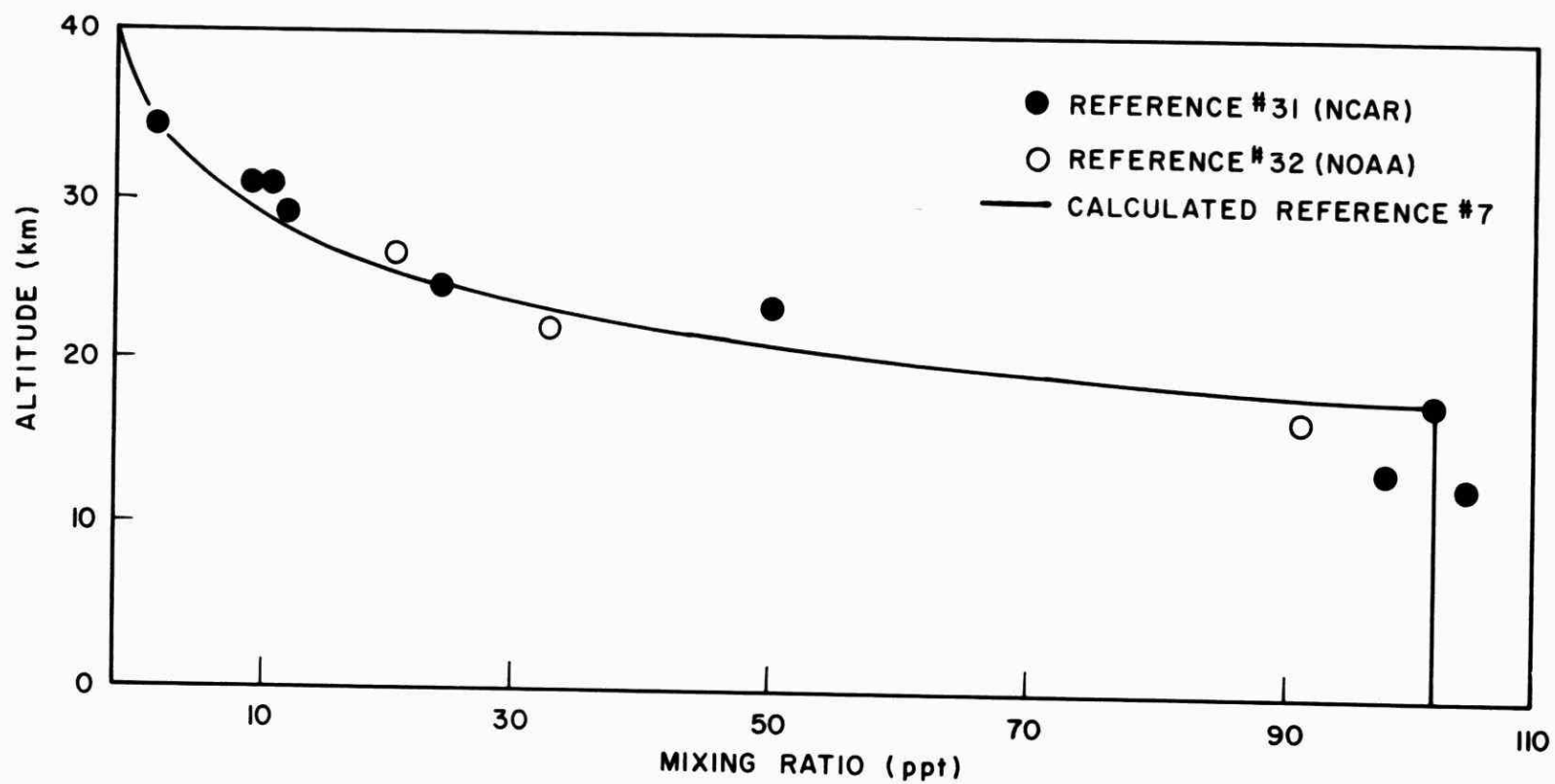


Figure 3: Stratospheric Measurements of F-11

b) Calculated vs. Observed Atmospheric FCC Burden

The present atmospheric burden of FCC's can be estimated from production figures if the following additional data are known:

- a) the fraction of production released to the atmosphere
- b) the average delay time between production and release to the atmosphere
- c) the average lifetime in the atmosphere

Such determinations have been carried out for F-11.⁷ These calculations estimated that 85 percent of F-11 production is used as aerosol propellants and another 5-8 percent in processes involving the foaming of polyurethane. A negligible amount is used in refrigeration.

An average delay time between production and loss to the atmosphere of six months was assumed. Various lifetimes were used for FCC's in the troposphere with the assumption that there is no delay period before each injected molecule becomes accessible to an unspecified sink. This would be true for tropospheric sinks having lifetimes in excess of one year but would not be correct for a stratospheric sink.

The integrated amount of F-11 produced to the end of 1972 is 1.7×10^9 kg of which about 10 percent may be assumed to be used in processes not involving release to the atmosphere. Using a six month time lag between production and release about 1.5×10^9 kg have been released to the atmosphere by the end of 1972. The cumulative amounts in the atmosphere would be

1.3, 1.2, or 1.1×10^9 kg for average lifetimes of 50, 30, or 20 years respectively.

The entire atmosphere contains approximately 9×10^{43} molecules (5.1×10^{18} cm² of earth's surface $\times 1.7 \times 10^{25}$ molecules cm⁻²) of which about 8×10^{43} molecules are in the troposphere. Distributing this F-11 load over the entire atmosphere results in levels for December 1972 of about 70 ppt for an infinite lifetime, 60 ppt for a 30 year lifetime, and 50 ppt for a 20 year lifetime.

Late 1972 measurements of F-11 indicate a mixing ratio of (61 ± 13) .⁴ Overall uncertainties in knowledge of industrial production rates for F-11 and measurement errors make precise comparisons impossible. In general, the presently observed amounts of F-11 in the atmosphere are inconsistent with atmospheric lifetimes shorter than 10 years. The 36 percent increase of F-11 from the measurements by Wilkniss et al⁴ over about a 15 month period (late 1972 to early 1974) is consistent with industrial production patterns which are the only known sources for FCC's.

Similar estimates for F-12 are more difficult to make. An appreciable fraction of F-12 is used as a refrigerant cooling fluid and delay times before eventual release to the environment are difficult to estimate. The amount presently in the atmosphere is also more difficult to measure because of the much lower sensitivity for F-12 compared to F-11 of electron capture detectors used in gas chromatographic assay. However, measurements indicating⁶ mixing ratios in 1973 for F-12 of 100 ppt roughly corres-

pond to atmospheric lifetimes comparable to or longer than that for F-11.

A substantial improvement in the average lifetime estimate for F-11 or F-12, as obtained from direct observations of the terrestrial concentrations, cannot be expected until a number of years have elapsed.

8. Atmospheric Sinks Other Than Photolysis

As indicated above, any tropospheric sinks which may be active should affect a lifetime for F-11 or F-12 of at least 10 to 15 years. Model calculations of FCC atmospheric lifetimes for a photodissociation sink vary depending on which set of eddy diffusion coefficients is used. F-11⁷ ranges from 41 to 85 years and F-12 from 53 to 205 years.

Even if the lifetimes of F-11 or F-12 are dominated by a stratospheric photolytic sink the participation of other atmospheric sinks could be important in determining safe levels of their use in the future. Several possibilities have been considered.

a) Reactions of F-11 and F-12 Photochemical Smogs

Experiments carried out by Pitts⁷⁹ in chambers simulating an urban photochemical smog have shown no chemical removal of F-11 or F-12. Under these conditions no major urban atmospheric sinks seem likely.

b) Oceanic Sinks and Rainout

Neither F-11 nor F-12 is very soluble in

water and neither is removed by rainout since they are observed to have long residence times in the troposphere. Their relative insolubility and chemical stability (especially toward hydrolysis)³⁴ indicate they will not be removed³ in the oceans. Measurements by Lovelock indicate equilibrium between the ocean surface and air mass. The amount of FCC's in these surface waters is a negligible fraction of the total amount in the atmosphere. Mixing to the deep ocean below the thermocline requires hundreds of years and hence is unimportant compared to transport of FCC's to the stratosphere and a photolytic sink.

Rates of hydrolysis in containers of FCC's and aqueous solutions are reported to be very slow^{10,35} for both F-11 and F-12. However, the homolytic cleavage of the C-Cl bond in F-11 in containers mixed with alcohol has been reported.^{36,37,38}

⁵
Su and Goldberg cite this possibility as an atmospheric reaction to account for their low values for the mixing ratio of F-11. However, this low value has not been confirmed by any other group and hence the importance of this reaction is open to question.

c) Biological Sinks

There is very little information concerning possible biological activity with FCC's. Hester

has indicated⁷ that preliminary experiments indicate soils and plants do not act as sinks for F-11 or F-12. In view of the recent anthropogenic origin of FCC's and their chemical inertness it seems highly unlikely that such biological sinks could occur.

d) Chemical Reactions with OH and O ('D)

Oxygen atoms are formed from photolysis of O_3 and O_2 . Photolysis of O_2 takes place in the upper stratosphere and produces two ground state $O(^3P)$ atoms. Ozone can photolyse in the stratosphere and troposphere ($\lambda < 310\text{nm}$) to form O_2 and an electronically excited oxygen atom $O('D)$. This is followed by chemical reaction or deactivation to $O(^3P)$.

³⁹
Pitts has found F-11 and F-12 to be less reactive than CH_4 to $O(^3P)$. However, he reports F-11 and F-12 to react rapidly with $O('D)$ having a rate constant of $3.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. This indicates a reaction on almost every collision.

The concentration of $O('D)$ is very low in the atmosphere except at high altitudes and hence the reaction of $O('D)$ with F-11 or F-12 does not compete well with photolysis at altitudes from 15 to 50 km. Below 15 km the rate of reaction of $O('D)$ and F-11 or F-12 is competitive with photolysis but both rates are negligible compared to vertical transport.

Abstraction of Cl from F-11 or F-12 by OH is endothermic and therefore will not occur at any alti-

tude. A displacement reaction could, in theory, occur but would be expected to have a high activation energy which would reduce its importance at stratospheric temperatures. Such displacement reactions have not been observed in laboratory experiments.

e) Dissociative Electron Capture

FCC's have relatively high cross sections for electron capture and hence the possibility of dissociative electron attachment should be considered.

Relatively large concentrations of electrons are produced in the ionized layers of the high atmosphere. These layers are so high above the altitudes at which photodissociation is important that they cannot act as sink for FCC's initially released in the troposphere and arriving at these ionized layers by vertical diffusion.

In the troposphere and lower stratosphere the concentration of electrons is kept low as a result of trapping by O_2 to form O_2^- . Any dissociative electron capture which may occur in the stratosphere would lead to the same fragments as from direct photodissociation since the initially formed Cl^- species would be subject to photoelectron detachment by radiation in the near ultraviolet wavelength region.

The cross section for electron capture for F-11 is about 100 times larger than for F 12. As

has already been discussed the tropospheric lifetime for F-11 is at least 10 years. Therefore, even if the only sink for F-11 is by electron capture then the corresponding lifetime for F-12 would have to be at least 10^3 years making this process negligible compared to vertical transport into the stratosphere.

f) Ion Molecule Reactions

In the stratosphere and troposphere, electrons which are formed by the passage of cosmic radiation, are very rapidly converted to O_2^- . O_2^- then, undergoes a series of very rapid reactions to form NO_3^- which can react with positive ions, undergo photoelectron detachment, or follow condensation reactions with H_2O to form a cluster ion $NO_3 (H_2O)_x^-$. Negative ion concentrations in the stratosphere have a maximum concentrations of 10^3 ions cm^{-3} and lower values in the troposphere with cluster ions being more important here.

If NO_3^- were to react with FCC's in the stratosphere at every collision the rate of reaction would be competitive with photodissociation. However, since NO_3^- has a high electron affinity, reaction by dissociative electron charge transfer with FCC's is unlikely.

The only energetically possible reactions are displacement reactions. Relatively few such reactions have been studied but there is no indication that such reactions occur. Reactions of

FCC's with ion clusters should be slower than with NO_3^- .

g) Heterogeneous Reactions with Aerosols

Aerosols are known to extend above the troposphere into the stratosphere, especially in the 15 to 21 km region.⁴¹ Adsorption of FCC's onto the surfaces of these particles without reaction cannot be important since this sink is not permanent. As these particles move into warmer regions of the troposphere the adsorbed FCC's would be released to the atmosphere chemically unchanged.

Neutron activation analysis of stratospheric aerosols for Cl has shown⁴² that transport by surface adsorption of Cl containing compounds cannot play a major role as a sink for ClX species due to the low quantities found.

It is possible that heterogeneous reactions involving aerosols and the various chlorine containing species which follow photodissociation of the FCC's in the stratosphere could terminate or shorten some of the chain reactions postulated to remove O_3 . Such effects should be largest in the 15 to 21 km altitude region where aerosol concentrations are highest.

Most of the ozone depletion is calculated to take place from 35 to 50 km. If chain termination is significantly catalysed by the presence of aerosols only in the 15 to 21 km altitude region, then this mechanism would have little affect on ozone concentrations.

h) Absorption in Polar Snow

33

Rasmussen has analyzed surface snow samples taken in the Antarctic for FCC's. Some preliminary experiments have shown FCC levels in the snow ranging from 5 to 20 times the mixing ratios of FCC's present in the overlying atmosphere. Further work is planned to examine the possibility of an antarctic sink for FCC's by analyzing core samples. However, the possibility of a significant sink here seems unlikely. The annual snowfall in the antarctic is quite low. 23 Rowland has estimated that even with a 20 times concentration of FCC's in the antarctic snow this sink would still be small compared to the oceans which themselves cannot account for more than about a one percent sink.

9. Photodissociative Sink for FCC's

a) Effective Wavelengths for Stratospheric Photolysis

All FCC's absorb light in the far ultraviolet. The absorption spectra have been reported by several 43,44,7 workers. Figure four presents the absorption spectrum of F-12. Absorption extends from 220 to at least 120 nm. Molecules at the outer edge of the atmosphere will receive radiation from the sun over this entire wavelength range. However, as FCC's diffuse up into the stratosphere they are selectively exposed to wavelengths which are able to penetrate the atmospheric components at higher altitudes. This filtering effect limits the rate of photolysis at various altitudes and reduces

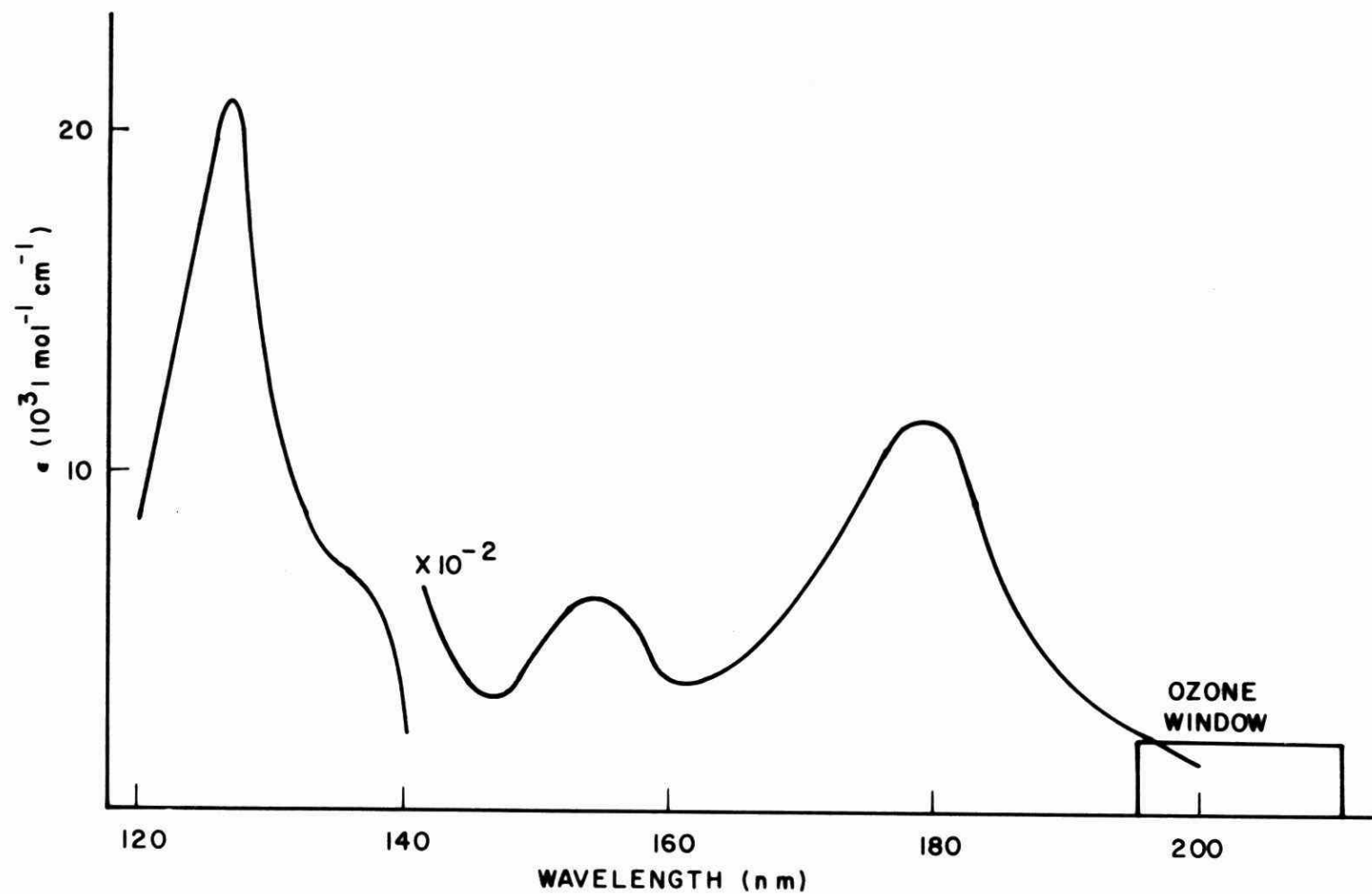


Figure 4: Absorption Spectrum of F-12⁷

photolysis in the troposphere to a rate negligible compared to vertical diffusion to the stratosphere.

Vertical diffusion in the stratosphere is relatively slow and the net effect is that FCC's are decomposed only by radiation in the relatively narrow band between 184 and 225 nm.⁷ This wavelength region represents a "window" between the more intense absorption by O_2 at lower wavelengths⁴⁵ and O_3 at longer wavelengths.

The incoming solar flux at any altitude can be determined using total flux data to the atmosphere (figure five) attenuated by absorption from O_2 and O_3 (figure six). The cross product of averaged solar flux at a given altitude and absorption cross sections indicate the wavelength range over which photolysis will occur (figure seven). Over 90 percent takes place between 195 and 215 nm for F-12. This is very similar to F-11 except for a slight shift to longer wavelengths and larger photodissociation coefficients.

The average lifetime for F-11 and F-12 can be determined at any altitude by combining the above calculated photodissociation coefficients with solar intensities (table seven). Below 20 km these photochemical lifetimes are so long that atmospheric diffusion processes are much more rapid and little photodissociation takes place before diffusion away from these altitudes occurs.

b) Temperature Dependence of Photolysis

Most laboratory data dealing with the photolysis of F-11 and F-12 have been obtained at room temperature. However, mid-stratospheric temperatures of around 230 K can be expected.

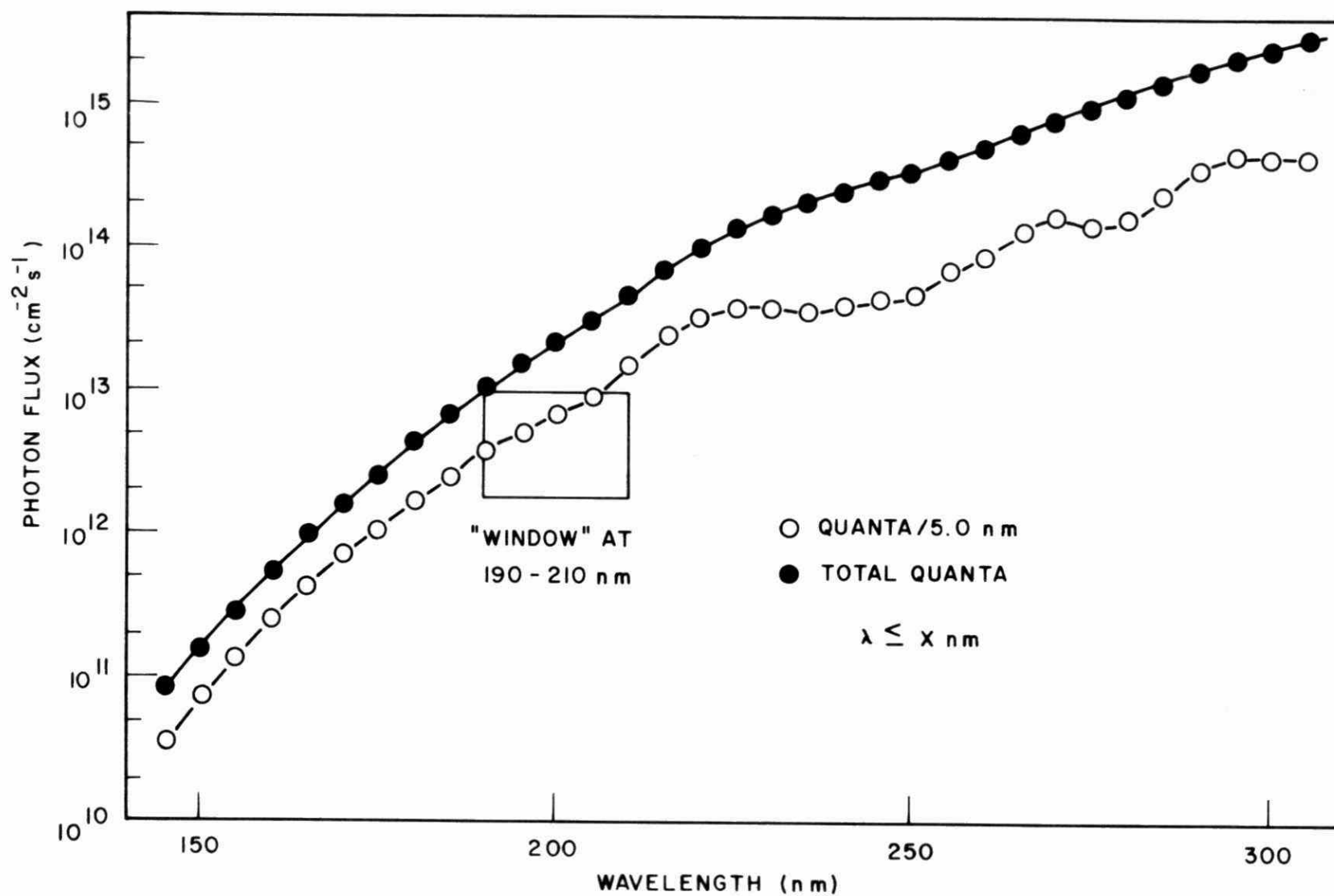


Figure 5: Solar Flux to the Atmosphere⁷

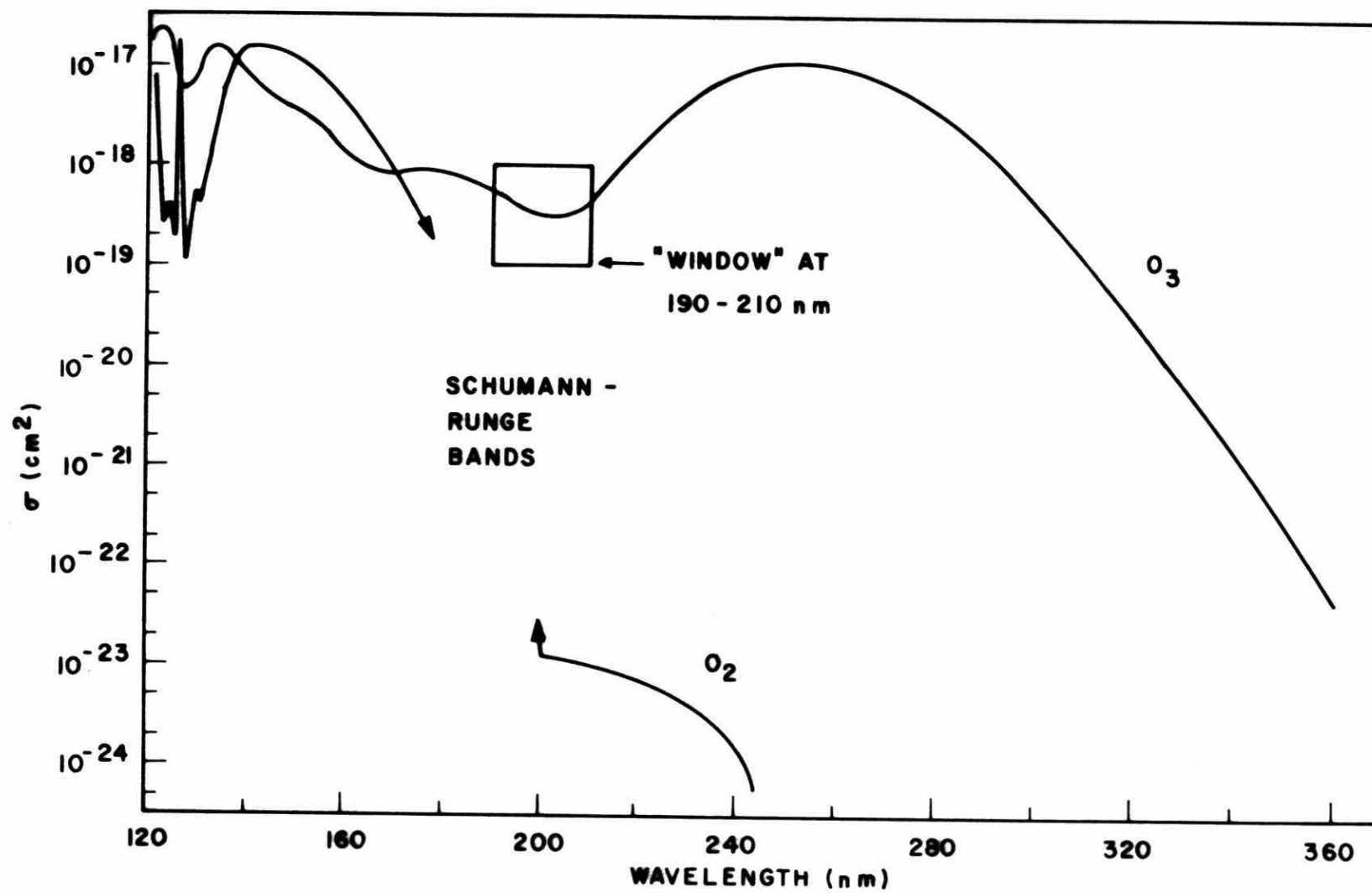


Figure 6: Absorption Spectra of O_2 and O_3

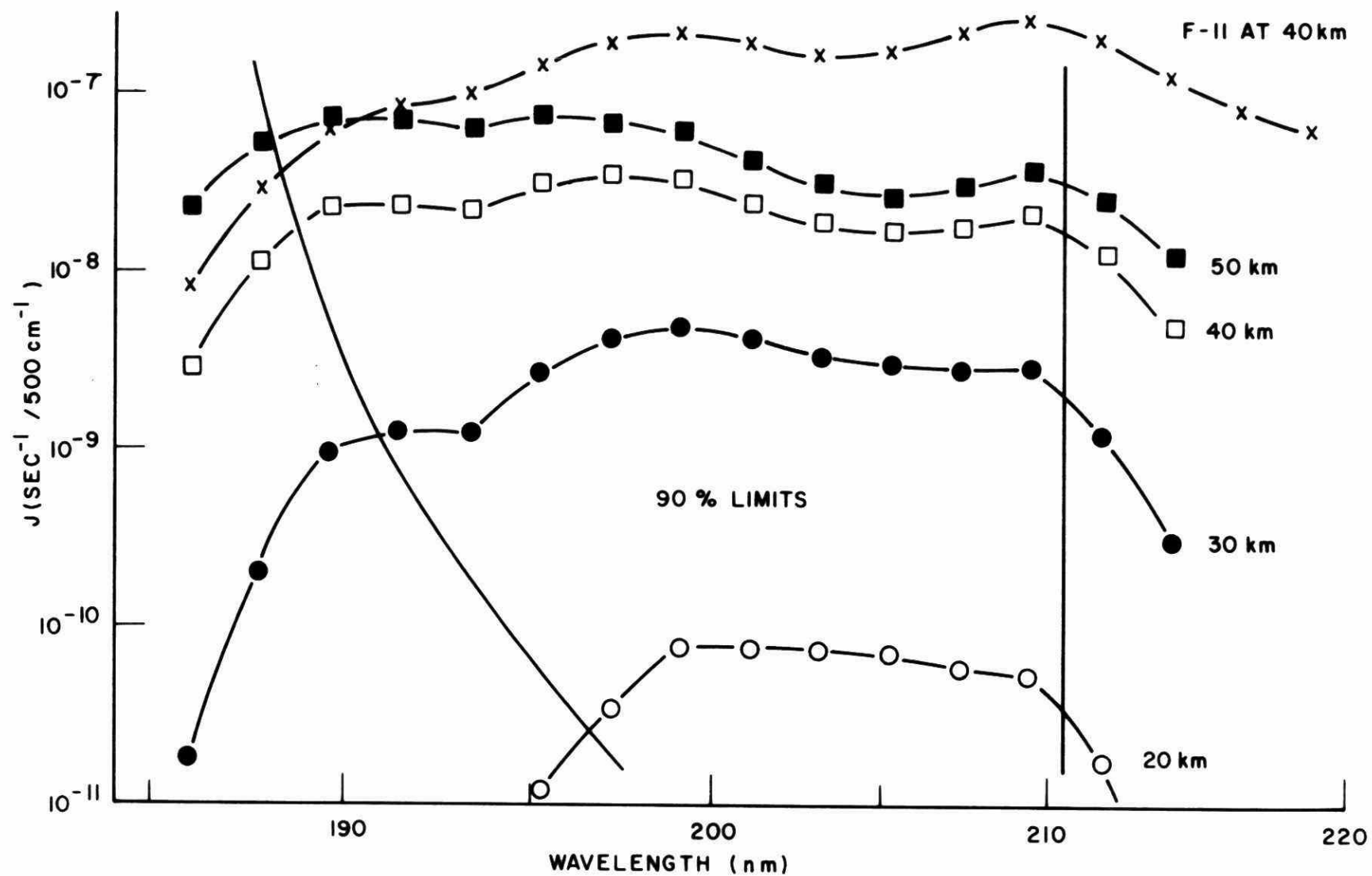


Figure 7: Solar Photon Absorption Coefficients for F-12

TABLE 7. CALCULATED AVERAGE PHOTODISSOCIATION LIFETIMES
FOR F-12 AND F-11 AT VARIOUS ALTITUDES⁷

Altitude (km)	Lifetimes(s)	
	F-12	F-11
10	1.2×10^{14} (4×10^6 yrs)	8.9×10^{12} (13×10^5 yrs)
20	2.1×10^9 (66 yrs)	2.1×10^8 (6.6 yrs)
30	2.9×10^7 (11 months)	3.4×10^6 (1.3 months)
40	3.3×10^6 (1.3 months)	4.0×10^5 (4.7 days)
50	1.4×10^6 (16 days)	1.8×10^5 (2.1 days)
Top of atmosphere	3.0×10^5 (3.5 days)	5.3×10^4 (15 hours)

46

Ausloos has studied the temperature dependence of the photolysis of FCC's and found a strong dependence, with a much lower photolysis rate at stratospheric temperatures than at room temperature. However his studies were carried out at 213.9 nm which is at the long wavelength end of the absorption spectra of the FCC's. Such long wavelength bands usually originate by transitions from thermally excited ground state levels of the molecule and normally show a strong temperature dependence.

23

Rowland has recently measured the temperature dependence of photolysis over the entire relevant spectral region for both F-11 and F-12. When the observed effects are integrated over the spectral range the effect of lower temperatures on the FCC lifetimes are not greater than 10 percent at any altitude.

c) Quantum Yields for Photodissociation of F-11 and F-12

Very few experiments have been carried out on the photolysis of FCC's. The initial step of absorption occurs in the lone pair of a chlorine atom. Energy relationships overwhelmingly favor the release of Cl rather than F.

The quantum yield for F-12 photolysis has been recently found to be unity using $\lambda = 184.9$ nm. The same value is inferred over the 195 to 215 nm band because of the absence of structure in the band and because all the energies are far above the minimum needed to rupture the C-Cl band.

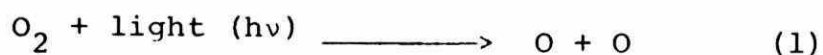
Measurements using F-11 show a constant quantum yield for decomposition in O₂ or in NO with widely varying

mixing ratios. This strongly suggests a quantum yield of unity in the stratosphere as well.

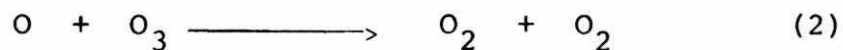
By analogy with CF_3 and CCl_3 the reaction of CF_2Cl and CFCl_2 with O_2 should give CF_2O and CFClO releasing either Cl or ClO . Experiments with F-12⁴⁹ indicate the formation of CF_2O but not CFClO . The ultimate fate of the third Cl atom for F-11 is uncertain but may be released by subsequent photolysis and chemical reactions.

10. Chemical Reactions in the Natural Stratosphere

The only important reaction which increases the concentration of O and O_3 in the stratosphere is the photolysis of O_2 by ultraviolet radiation with wavelengths less than 242 nm as in (1). A prime mechanism for removal of odd oxygen ($\text{O} + \text{O}_3$)



in the stratosphere is direct reaction of O and O_3 as in (2). The bimolecular reaction of two molecules of O_3 as in (3) is

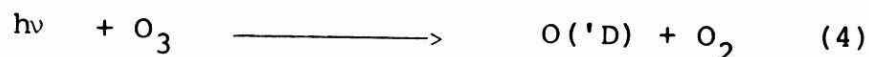


not significant.

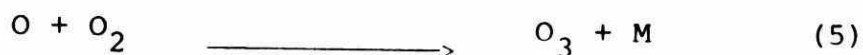
A variety of reaction sequences have been discovered involving odd-electron species such as HO_x (H , OH , HO_2), NO_x (NO , NO_2), ClO_x (Cl , ClO , ClOO , OClO) and FO_x (F , OF , FO_2) which can accomplish either reaction (2) or (3) by a catalytic sequence summing to one of these reactions.

The absorption of ultraviolet radiation by O_3 results

in the formation of O atoms as in (4). The

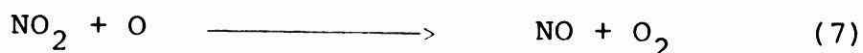


reaction of O and O_2 , as in (5) then reforms O_3 . This recombination reaction releases energy to the stratosphere.

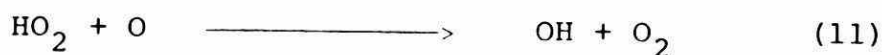
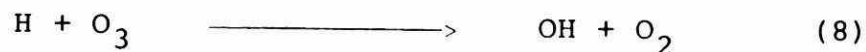


The combination of reactions (1), (2), (4) and (5) are responsible for the substantial rise in temperatures (210 K to 274 K) occurring with altitude from 15 to 50 km.

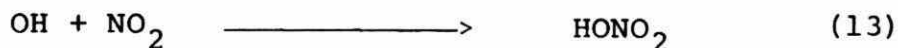
Reactions (1), (2), (4) and (5) are those originally suggested by Chapman⁵⁰ to control the amount of stratospheric ozone. More recent work suggests that the reactions of NO_x result in the greatest net removal of odd oxygen in the stratosphere as in reactions (6) and (7).



Several similar reaction sequences for HO_x have also been identified as in (8) to (12). However, their net contributions are considerably less important than the NO_x cycle for odd oxygen removal as revealed by a detailed study of individual^{51,52} rate constants.



Propagation of these chain type reactions is terminated if a relatively non-reactive free radical is formed (such as HO_2), or two free radicals react to form even electron species as in (13) which illustrates the cross termination

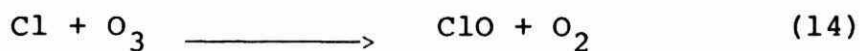


of two chains. Such a terminating molecule can be forced into the reaction sequence again by its photolysis.

11. ClO_x Chain for O_3 Decomposition

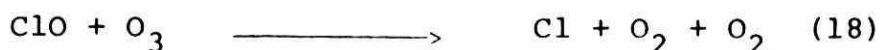
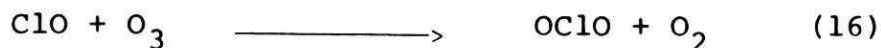
The possibility of a stratospheric sink for FCC's and an ensuing chain reaction involving ClO_x and O_3 was first suggested by Molina and Rowland.⁵³ Since then several publications have appeared attempting to give a quantitative estimate of the effects of various emission rates of FCC's at ground level (see references 54, 55, 7, 56, 57, 58, 59, 60). Calculations have also been carried out to determine the effects of stratospheric injection of HCl expected from the proposed U.S. space shuttle^{61, 62, 63} which uses NH_4ClO_4 as a fuel.

The most important chain process in the stratosphere for ClO_x involves the Cl/ ClO chain as in (14) and (15).



Both of these take place with essentially zero activation energy and high collision efficiency. Reaction (14) is about 2.3×10^3 times faster at mid-stratospheric temperatures than the reaction between NO and O_3 while reaction (15) is about six times faster than the reaction of NO_2 and O atoms.

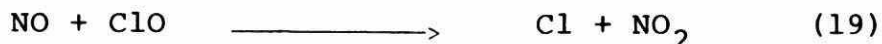
The possible reaction of ClO and O₃ could lead to three different sets of products as in (16), (17), and (18).



Reactions (17) and (18) are equivalent in effect since ClOO will rapidly convert to Cl and O₂. OClO is highly unstable and should photodissociate rapidly in the stratosphere.

The reaction of ClO and O₃ has been found to be very slow at room temperature with an activation energy of 8 to 13 kJ mole⁻¹. Therefore this reaction and the OClO molecule are not expected to be important in the stratosphere.

The cross chain reaction between ClO and NO can occur as in (19). The ultimate consequences of this



reaction depend on the fate of NO₂. If NO₂ reacts with O as in (7) then a net removal of odd oxygen results. The competition between NO and O for ClO favors NO at lower altitudes due to the drop in O concentrations with decreasing altitude. However, the rate of reaction (7) is also slower for the same reason. Consequently at altitudes where NO competes with O for ClO the primary fate of NO₂ is photolysis to NO and O and hence the initial attack of Cl on O₃ finally leads back to an O atom with no net change in O atom concentration. The effect of reaction (19) is thus to reduce the net rate of odd oxygen removal.

The bulk of odd oxygen depletion by ClO_x occurs at 35 km or higher. Calculations indicate that at 45 km Cl reacts with O_3 in 0.3 seconds, ClO with O or NO (86 percent with O) every 14 seconds, and about 4 cycles of reactions (14) and (15) are completed each minute removing 32 equivalents of odd oxygen.

This chain continues until terminated by a side reaction forming HCl. The frequency of this side reaction is 1 in 2,600 cycles at 45 km indicating an average chain lifetime of 10 hours. The rate of re-starting the chain at 45 km by attack of OH on HCl is estimated to be 2.4 days. Thus, each ClX entity removes about 5,000 odd oxygen species every three days at 45 km and continues to do so until it diffuses to another altitude with eventual permanent removal at the troposphere.

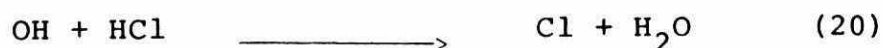
The temporary termination of Cl atom chains is accomplished by hydrogen abstraction by Cl atoms. Sources of H atoms include such molecules as CH_4 , H_2 , H_2O_2 , HNO_3 , HO_2 etc. The attack of Cl on H_2O is endothermic by 10 kcal mole⁻¹ and therefore is not important.

A combination of atmospheric abundance and reaction rate constants makes H abstraction from CH_4 , HO_2 and H_2 the dominant processes. Abstraction of a H atom from H_2 is only about 20 to 30 percent as important as for CH_4 . If the rate of abstraction from HO_2 is collisionally controlled it could compete with CH_4 for Cl. However, geometrical considerations alone make collisional efficiencies near unity highly unlikely. This rate constant has not been measured.

The rate constant for the reaction of Cl with OH to form HCl and O has not been measured but the activation energy for the reverse reaction has been found to be from 16 to 30 kJ/mole. Since the forward reaction is 3 kJ/mole exothermic the reverse reaction must have an activation energy of at least 13 kJ/mole and hence would be unimportant at stratospheric temperatures.

The possibility of important Cl reactions with other hydrogenous compounds is highly unlikely. From the temperature dependence of the reaction rate constant for the reaction of Cl with CH₄, the collision efficiency of Cl with CH₄ at mid-stratospheric temperature is about 10⁻⁴ and the relative abundance of CH₄ is approximately 10⁻⁶. Consequently, even at unit collisional efficiency, only species having relative abundances of 10⁻¹⁰ could have a comparable effect to that of CH₄ in terminating Cl atom chains. Except for HO₂ and H₂ most species either fall below that concentration level or the abstraction reaction has a substantial activation energy or both.

HCl acts as sink for Cl species in the stratosphere and its formation halts the catalytic chain reaction for destruction of O₃. The downward diffusion of HCl to the tropopause where it is removed by weathering processes constitutes a permanent sink for Cl species. In competition with this is the photolytic dissociation of HCl and attack by OH radicals as in (20). At most altitudes in the stratosphere

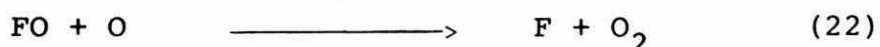
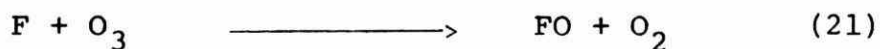


reaction (20) dominates. Consequently, HCl acts as temporary sink for Cl species and attack by OH results in the re-starting of the Cl/ClO chain reaction for odd oxygen removal.

The rate constant for reaction (20) has been measured and recent experiments⁶⁴ have found an activation energy⁷ lower than that originally used. The result is that the rate constant for reaction (20) is larger at stratospheric temperatures than originally thought.

Other chain terminating reactions are either slow compared to H abstraction from CH₄, H₂, and HO₂ or produce chemical species which are either not known (and may well not be stable) or have a strong absorption spectrum in the near ultraviolet and/or visible wavelength regions leading to very short photodissociative lifetimes.

With the introduction of F-11 and F-12 to the stratosphere and subsequent photodissociation there, is the undetermined possibility of the release of F atoms. Once formed, a chain reaction involving F and FO for the reduction of odd oxygen can take place as in (21) and (22). However, the abstraction of hydrogen atoms



from CH₄ or H₂ is much faster by F than Cl. Once formed, the molecules of HF are strongly bonded and are not attacked by OH due to the endothermicity of the reaction. Photodissociation is also slow due to a low absorption cross section in the critical 180 to 220 nm region. Thus, in contrast to Cl, chain reactions for the reduction of odd oxygen species involving F are not important.

12. Atmospheric Modeling

Mathematical models which simulate atmospheric motions

are currently being developed for systems of one, two and three dimensions introducing vertical, longitudinal, and latitudinal motions in that order. The current 3-dimensional models are sufficiently complicated that only a very limited number of chemical reactions can be included.

Most published treatments involve only one-dimensional diffusion models in which vertical mixing is treated using the concept of globally averaged vertical eddy diffusion coefficients. The same coefficient is used for all gases and is obtained as an adjustable parameter in a best fit for mixing patterns observed for species in the real atmosphere. Examples of various choices of eddy diffusion coefficients are illustrated in figure eight.

Such models do not predict latitudinal or longitudinal variations.

Because of the long time scale involved for stratospheric diffusion, calculations for the troposphere show an essentially imperceptible concentration gradient below the tropopause. Accordingly, an assumption of rapid and complete mixing is used for the troposphere. The tropopause is considered to be a permanent and immediate sink for downward diffusing dissociation products.

Several workers have published model calculations to indicate the possible effects of ClX species in the stratosphere and the consequences of continued FCC release to the troposphere. These are mostly one-dimensional calculations, including both steady state, time independent calculations, and complete time dependent solutions (see references 7, 53, 54, 57, 63, 59, 58, 60, 61).

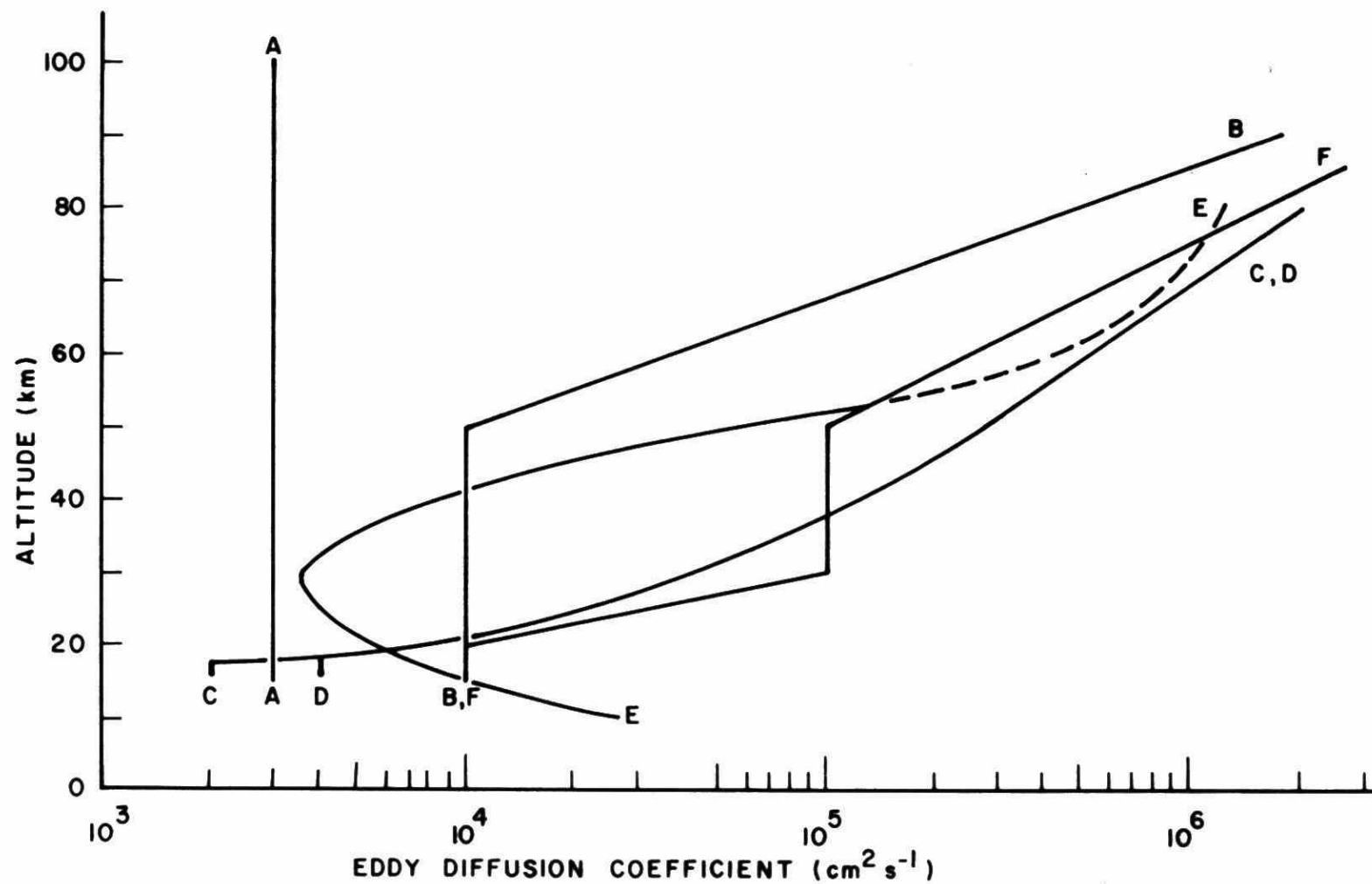


Figure 8: Eddy Diffusion Coefficient Profiles⁷

a) Steady State Calculations

For steady state conditions time independent-solutions can be obtained. Using solar flux data and diffusion coefficients as a function of altitude combined with ground FCC emission rates and absorption cross sections, the vertical steady state concentrations of FCC's can be calculated as well as the rate of decomposition at any altitude.

The rate of FCC loss can be equated to the injection rate of ClX at any given altitude (figures nine and ten). Since the attainment of chemical equilibrium in the stratosphere is much more rapid than vertical diffusion, the distribution of ClX species at any given altitude reaches a steady state before moving to another altitude. In the calculations fixed average concentrations of non-ClX species (HO_x , NO_x , O and O_3) such as those reported in references 51 and 65 are used (figure 11, 12 and 13).

This approach is suitable to predict steady state profiles for FCC's in the stratosphere and to roughly indicate relative contributions to odd oxygen removal rates by NO_x and ClO_x reaction chains once steady state has been achieved (figure 14). However, it does not provide any information on the time dependent effects and ensuing consequences of various possible controls of FCC emissions.

The time taken to reach equilibrium for a given rate of release for FCC's is considerable since, depending on the choice of diffusion coefficients, steady state calculations show lifetimes for F-11 ranging from 29 to 85 years and for F-12 from 53 to 205 years ⁷ (table eight). It is essential to calculate effects during this time period.

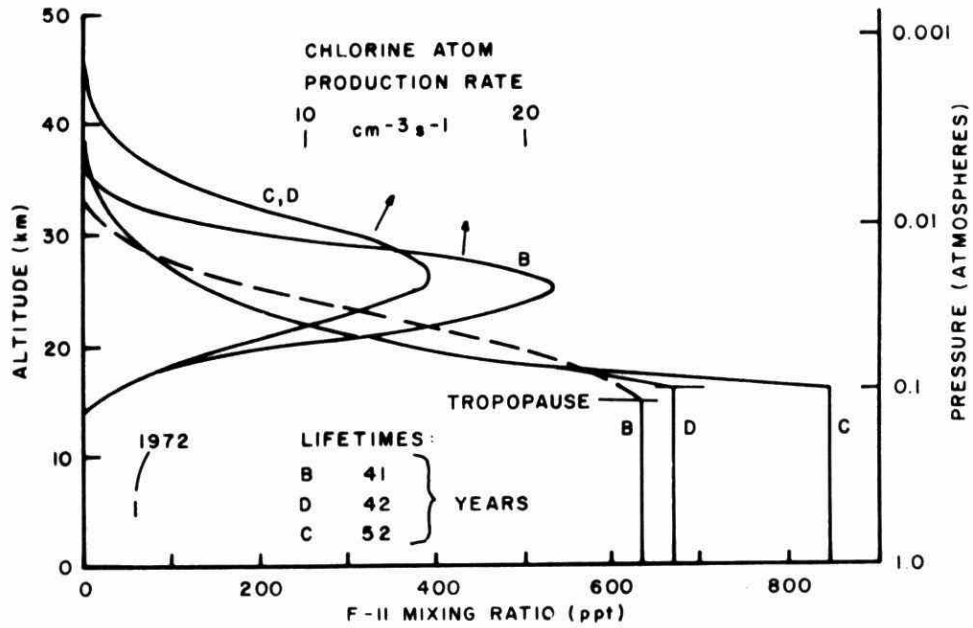


Figure 9: Steady State F-11 Concentration Profile and ClX Injection Rate⁷
(Based on 1972 F-11 Production Rates)

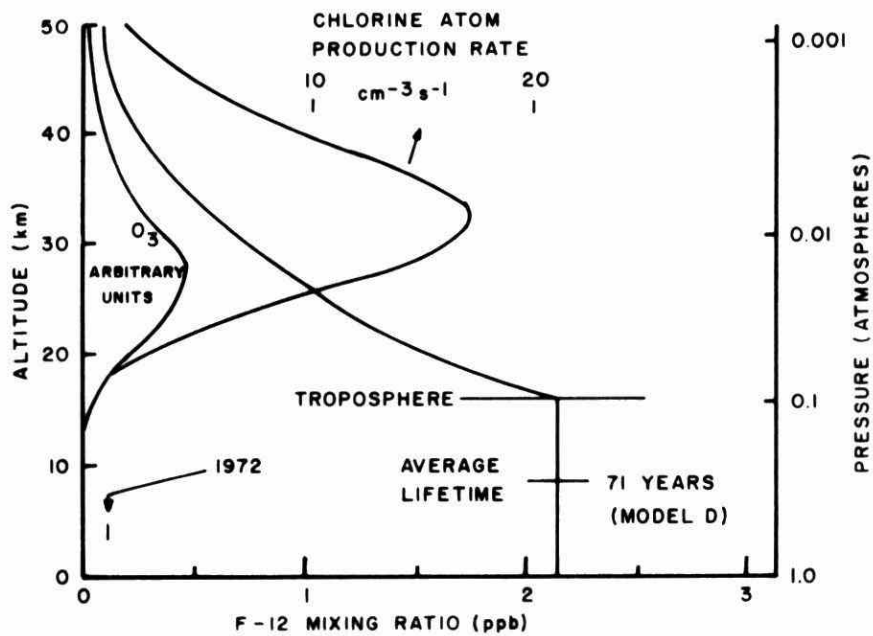


Figure 10: Steady State F-12 Concentration Profile and ClX Injection Rate⁷
(Based on 1972 F-12 Production Rates)

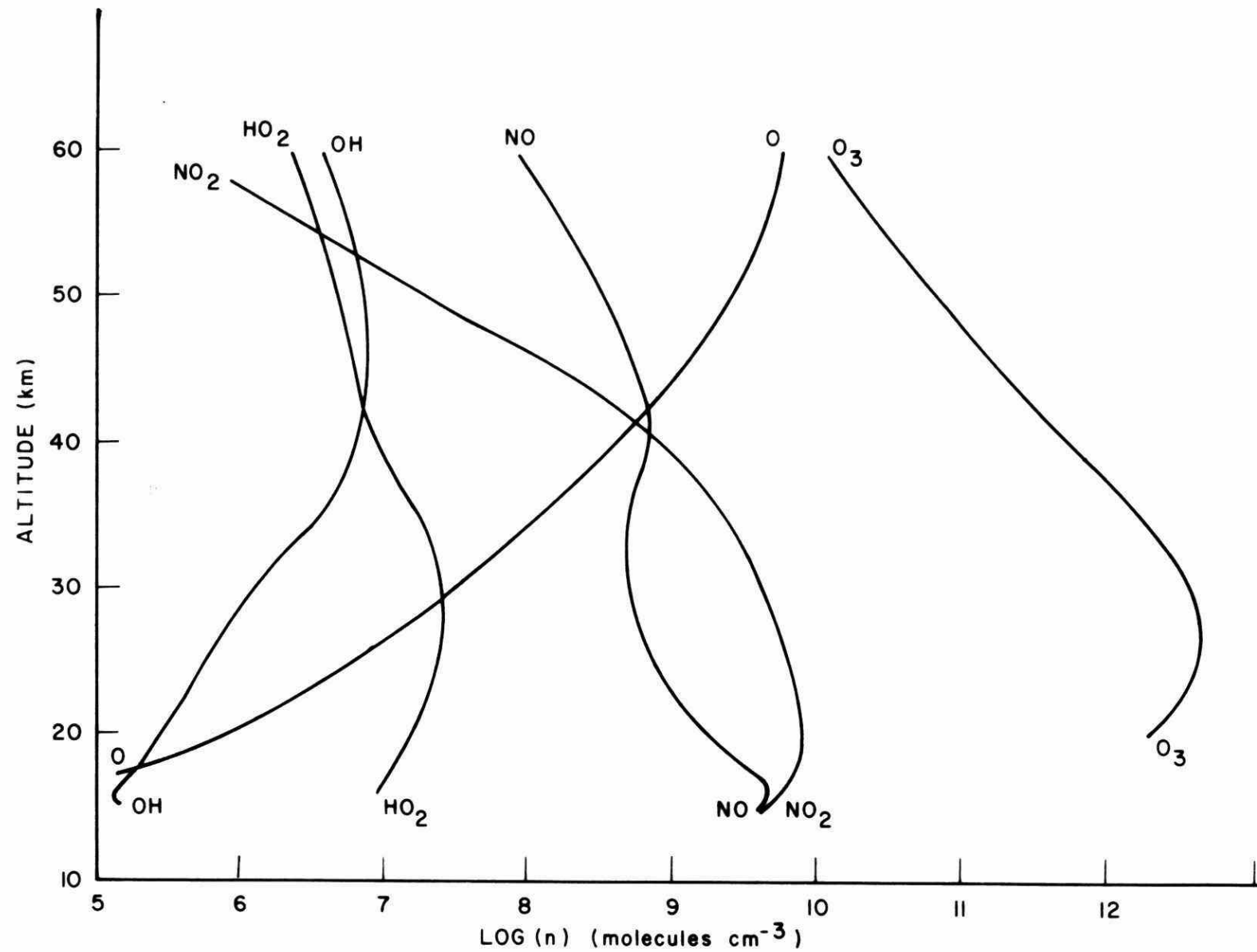


Figure 11: Assumed Steady State Concentration Profiles of Reactive Species in the Stratosphere⁷

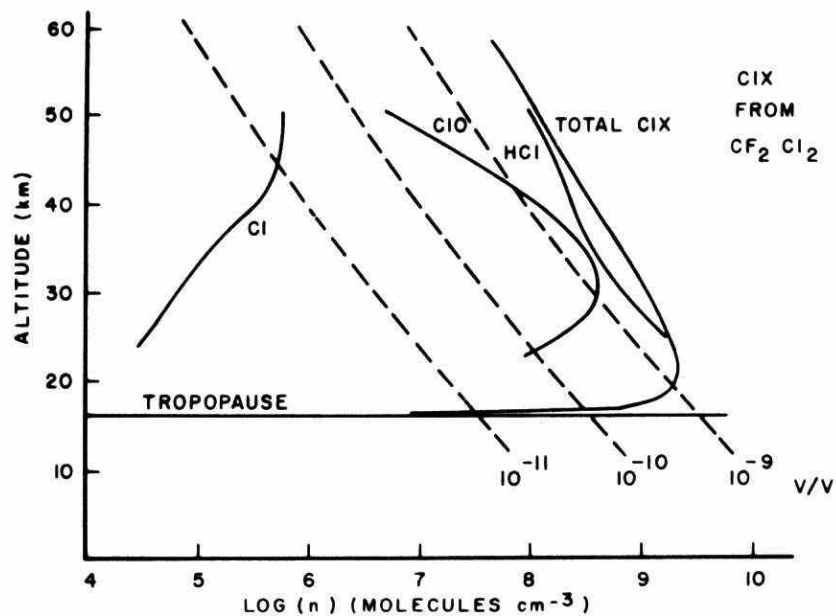


Figure 12: Steady State ClX Concentration Profiles Based on 1972 F-12 Production Rates⁷

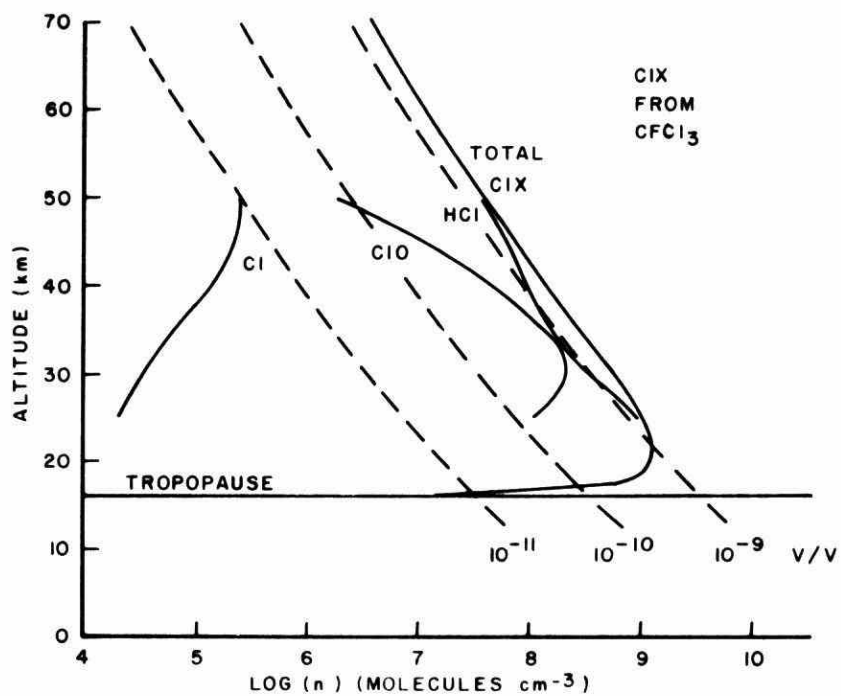


Figure 13: Steady State ClX Concentration Profiles Based on 1972 F-11 Production Rates⁷

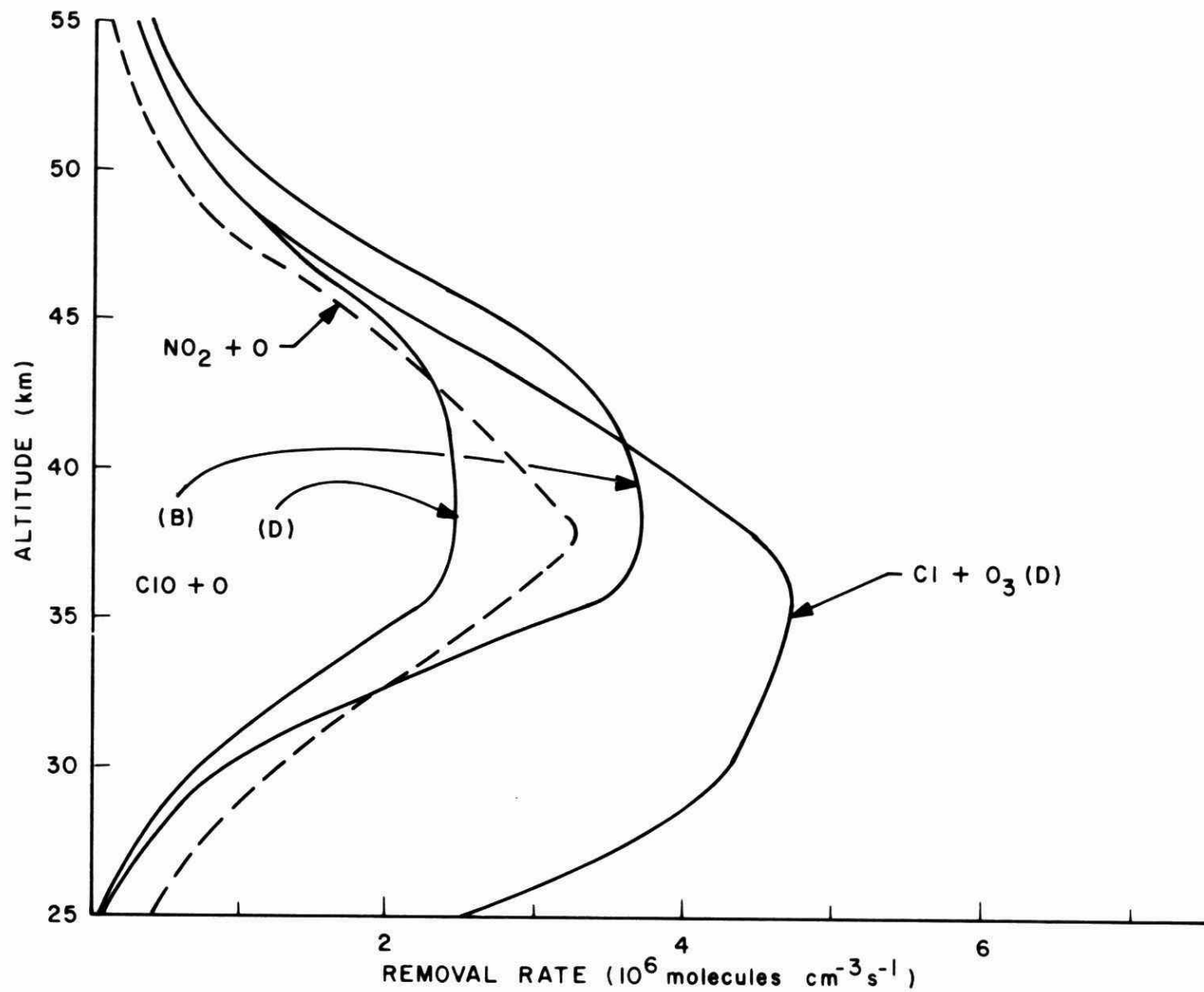


Figure 14: Steady State Removal Rates of Odd Oxygen by Various Reactions⁷
(Based on 1972 Production Rates of F-11 and F-12)

TABLE 8. CALCULATED AVERAGE ATMOSPHERIC LIFETIMES
FOR F-12 AND F-11 WITH DIFFERENT EDDY
7
DIFFUSION COEFFICIENT MODELS

LIFETIME (IN YEARS)

MODEL	A	B	C	D	E	F
F-11	85	41	52	42	60	29
F-12	205	102	82	71	160	53

In addition, this approach can only accurately predict steady state effects when they only produce a small effect on the chemical system. For large effects the assumed "fixed" average distribution of non-ClX species is significantly altered.

Second order changes should also be considered. O_3 is formed as a result of O_2 photodissociation at higher altitudes in the stratosphere. This process is not effective at lower levels due to attenuation of solar flux as a result of absorption by O_2 and O_3 above. If ClX injection causes a sharp drop in the O_3 mixing ratio then O_2 photolysis at lower altitudes will be enhanced.

Further, changes in O_3 concentrations, affecting the radiation balance of the stratosphere, will also change its temperature profile which in turn affects reaction rates for those reactions having significant activation energies. Such "self-healing" and feedback effects need to be included in any model used to obtain quantitative results.

b) Time Dependent Calculations

Several groups have calculated the expected effects from FCC's as a function of time through a temporal solution to the diffusion and chemical equations.

In these calculations mixing in the troposphere is assumed to be instantaneous on the time scales appropriate to stratospheric diffusion. The troposphere is assumed to be a perfect sink for ClX species which fixes the concentration of ClX at zero at the tropopause. Numerical solutions are obtained by a stepwise, small finite difference technique.

The results obtained depend on which sets of eddy diffusion coefficients, solar flux profiles, and rate constants for key chemical reactions are chosen. Despite varying assumptions, independent groups have reached results which agree with each other within a factor of two.

All one dimensional time dependent models reported indicate the following characteristics.

There is a considerable time delay between a change in FCC production rates and the ensuing effect on the balance of odd oxygen in the stratosphere. This delay, or induction period, varies from two to five years depending on the model used. The reason for this is partly due to the delay period between production and release to the atmosphere, but mainly because of the slow diffusion rates in the stratosphere.

Following a halt in FCC production the recovery of O_3 levels is very slow. For example, if projected production patterns for FCC's through to 1990 are realized and at that point production ceases then the peak depletion of ozone will not appear until the year 2000. It could then take at least 150 years for O_3 to return to 1975 levels. The amount of O_3 depletion already suffered is estimated to be from 0.6 to 1.3 percent and, even if production were to halt today, there would be a peak reduction of from 1.3 to 3 percent. The predicted effects of various models are illustrated in figures 15 to 18.

It should be pointed out that these are globally averaged expected results. Local effects could be more severe. Attempts at two dimensional modeling ^{66,23} have indicated about a factor of two higher in globally averaged O_3

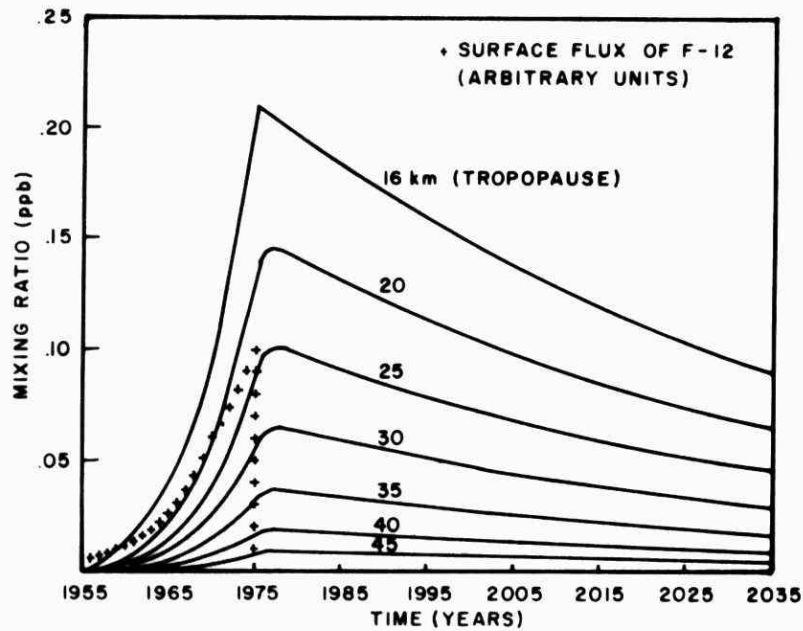


Figure 15: Time Dependence of the Concentration Profile of F-11 For a 1975 Production Halt⁷

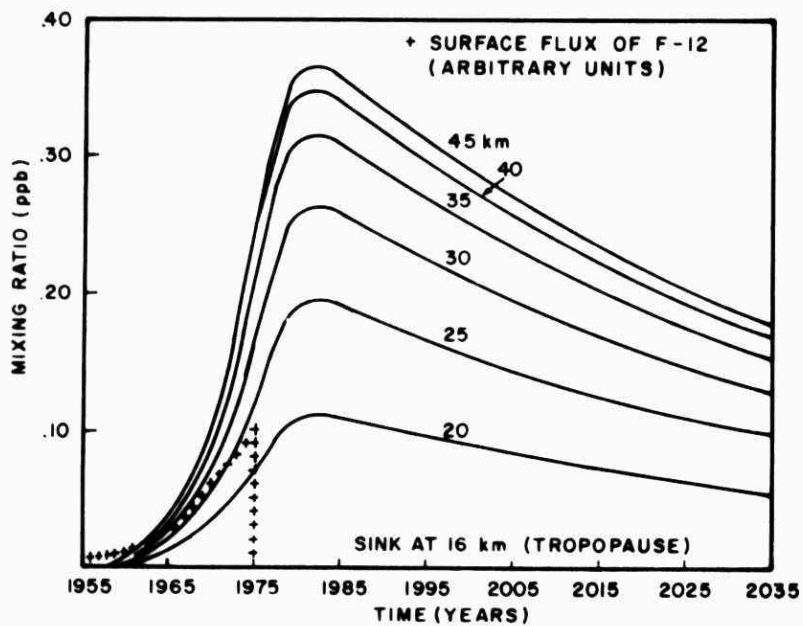


Figure 16: Time Dependence of the Concentration Profile of ClX For a 1975 Production Halt⁷

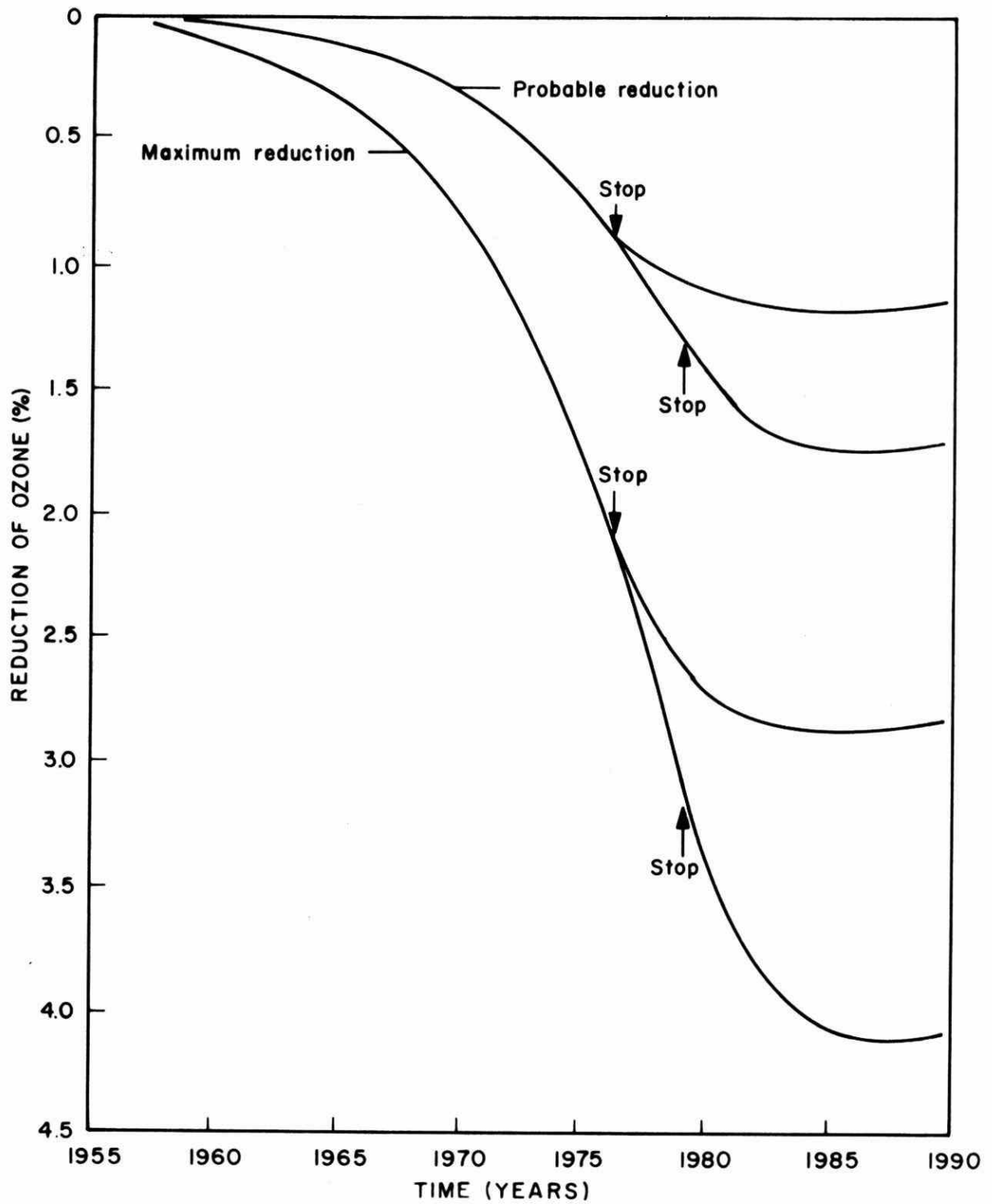


Figure 17: Ozone Depletion as a Function of Time (1955 to 1990) For Production Stops In 1976 and 1979⁸⁰

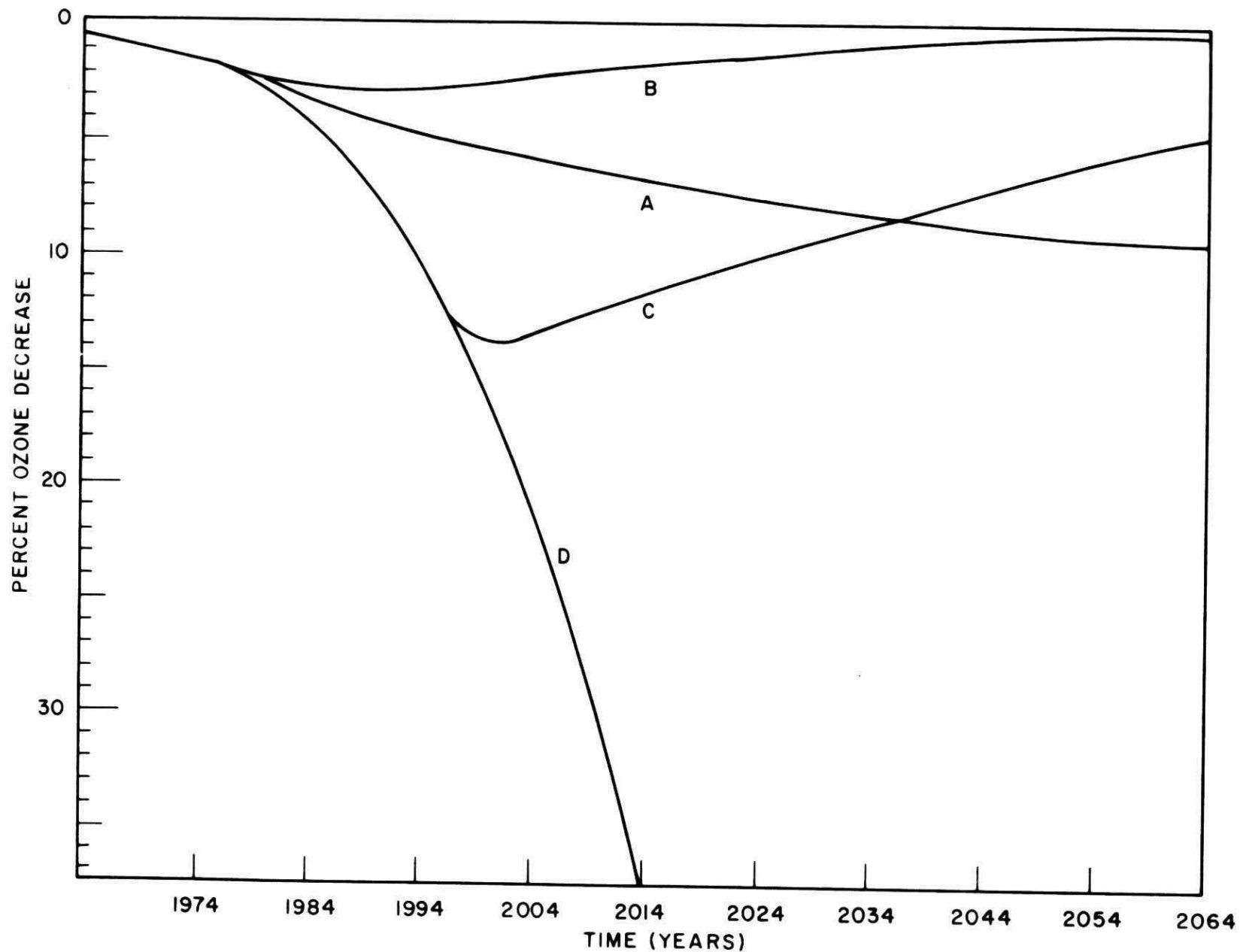


Figure 18: Ozone Depletion as a Function of Time (1964-2064) Expected For Various Control Strategies⁶⁰ (A. Production Constant at 1972 Level; B. Production Halt In 1978; C. Production Halt In 1995; D. Production Unchecked at 10% per year)

depletion. These models are subject to a higher degree of uncertainty than one dimensional models (figure 19 and 20).

13. Ozone Variability-Observed Trends

The ozone natural equilibrium concentration fluctuates considerably on a daily basis, between seasons, annually, and with latitude. Differences between day and night range from 10 to 20 percent, and seasonal changes in southern Canada can be as large as 20 percent. The differences in latitude from Toronto to Miami leads to a decrease in total vertical column, ozone concentration of 10 to 25 percent, depending on the season (figure 21).

Biennial variations of 2 to 3 percent have been observed while long term trends at Tronso in Norway⁶⁷ show a distinct eleven year cycle correlating with the well known sun spot cycle. Variation in sun spot activity is accompanied by variation in the amount of ionizing radiation from the sun reaching the Earth's atmosphere. This leads to a fluctuation in the amount of NO_x formed as a result of the passage of this radiation into the upper atmosphere which in turn influences the dynamic balance of ozone. The eleven year cycle of ozone concentrations is greatest at higher latitudes, presumably due to the effect of the Earth's magnetic field in concentrating incoming ionizing particles to the poles (figure 22).

It is interesting to note that an ozone peak from the eleven year cycle expected during 1960 was strongly distorted. This observation can be explained as the result of atmospheric testing of nuclear weapons during this period

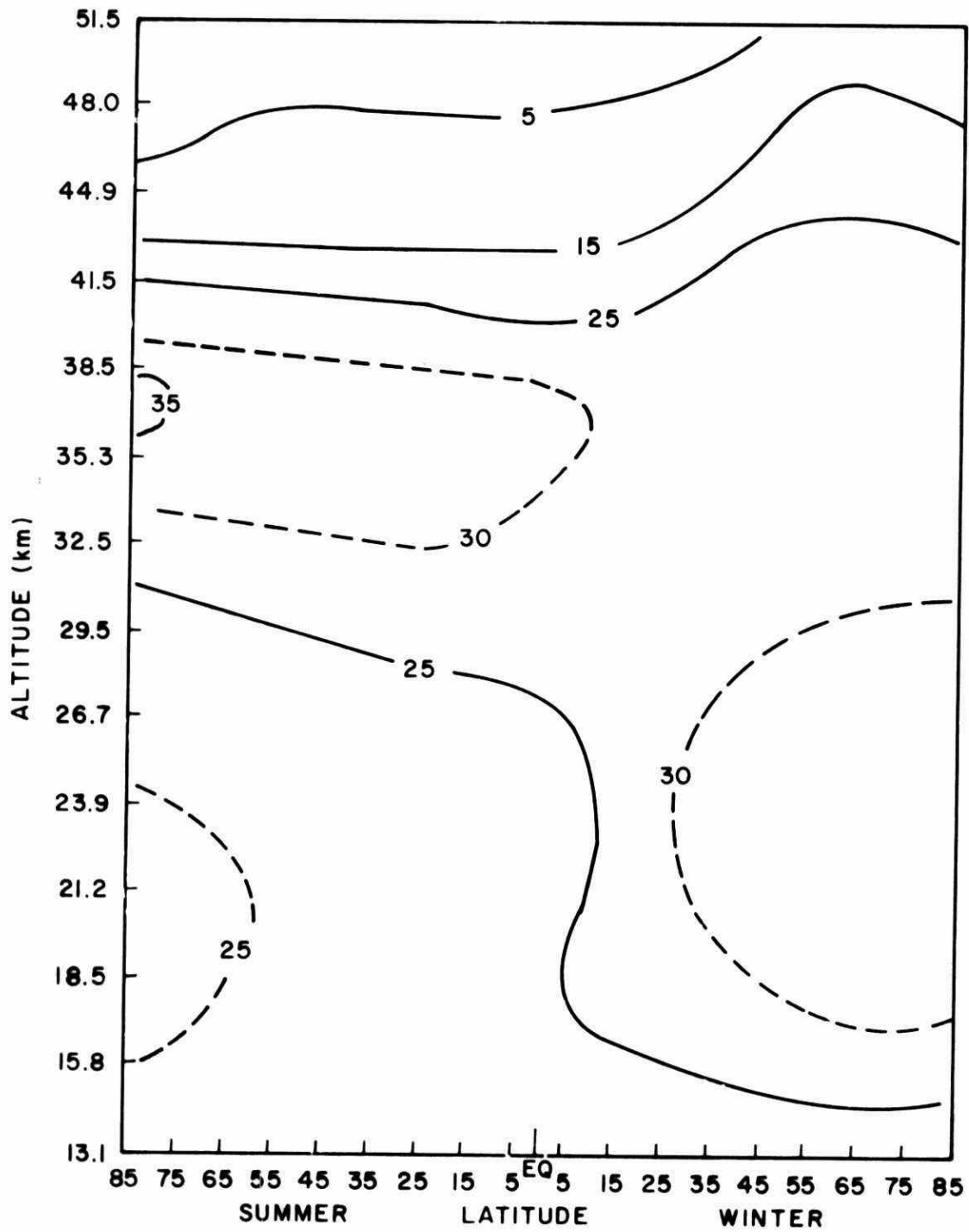


Figure 19: Ozone Depletion as a Function of Altitude and Latitude for a Steady State 1972 Production Rate of FCC's⁶⁶

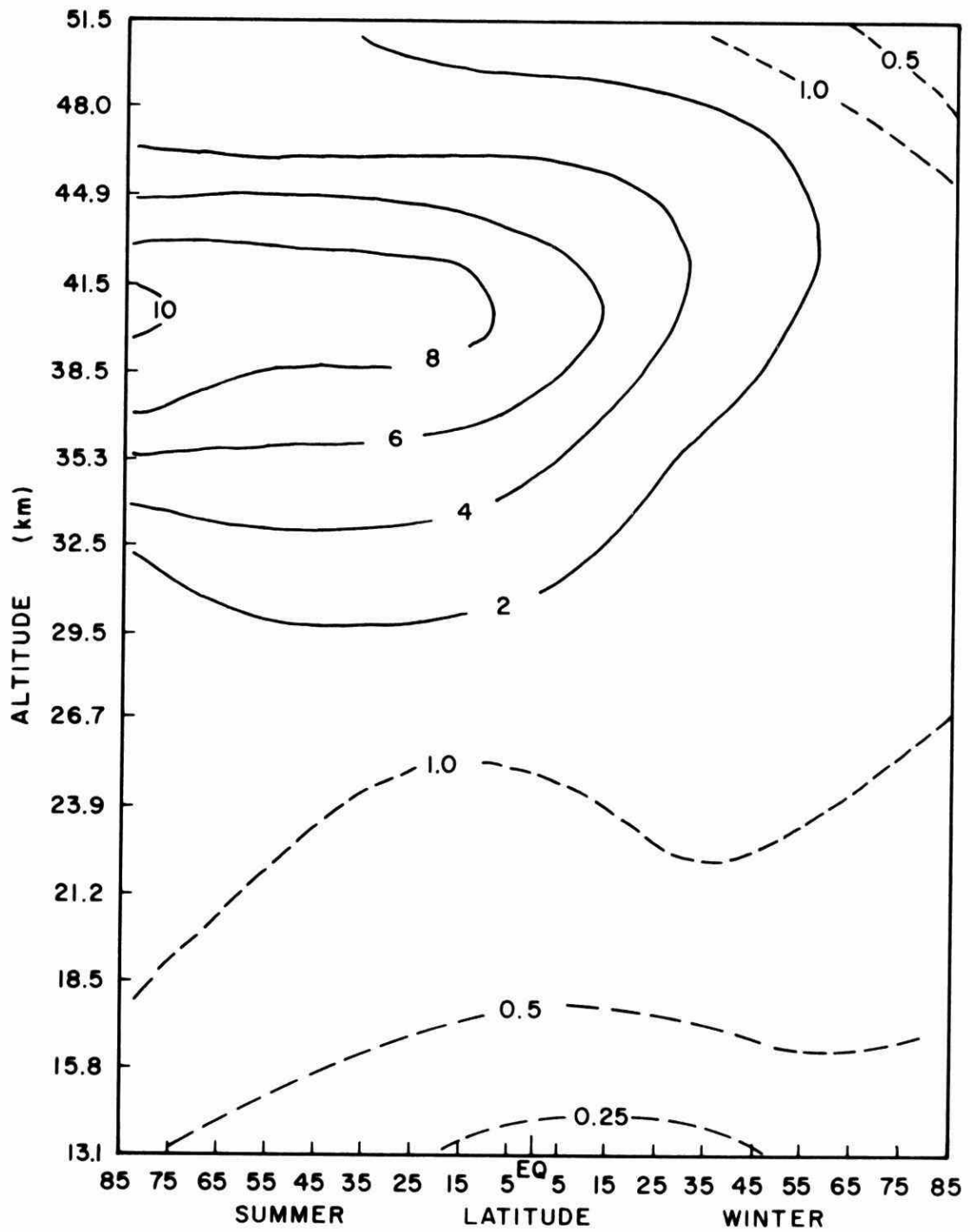


Figure 20: Temperature Drop (K) as a Function of Altitude and Latitude For a Steady State 1972 Production Rate of FCC's⁶⁶

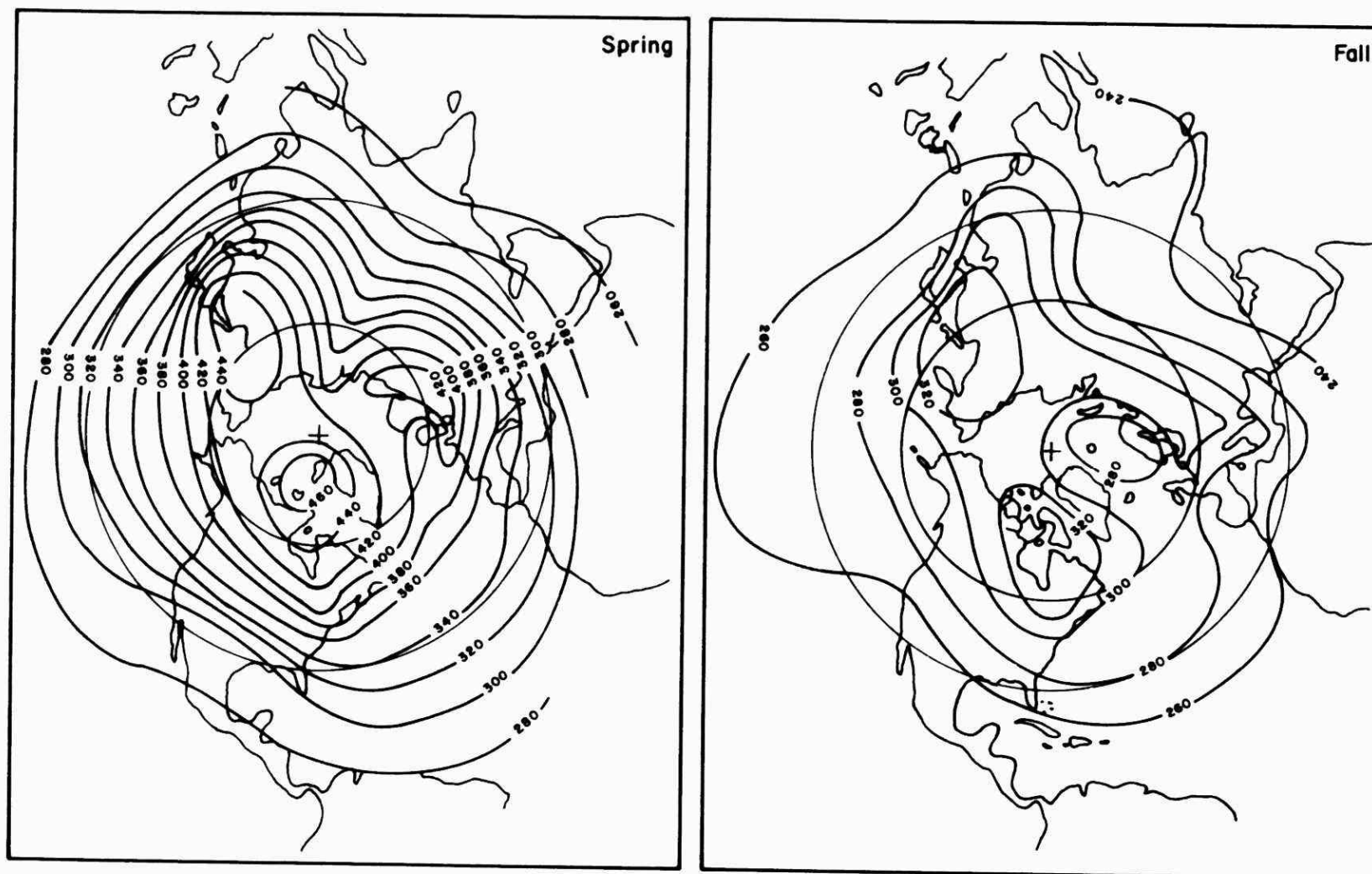


Figure 21: Typical O_3 Isopleths Over The Northern Hemisphere-Spring and Fall (Contours are in miliatmosphere-centimeters)

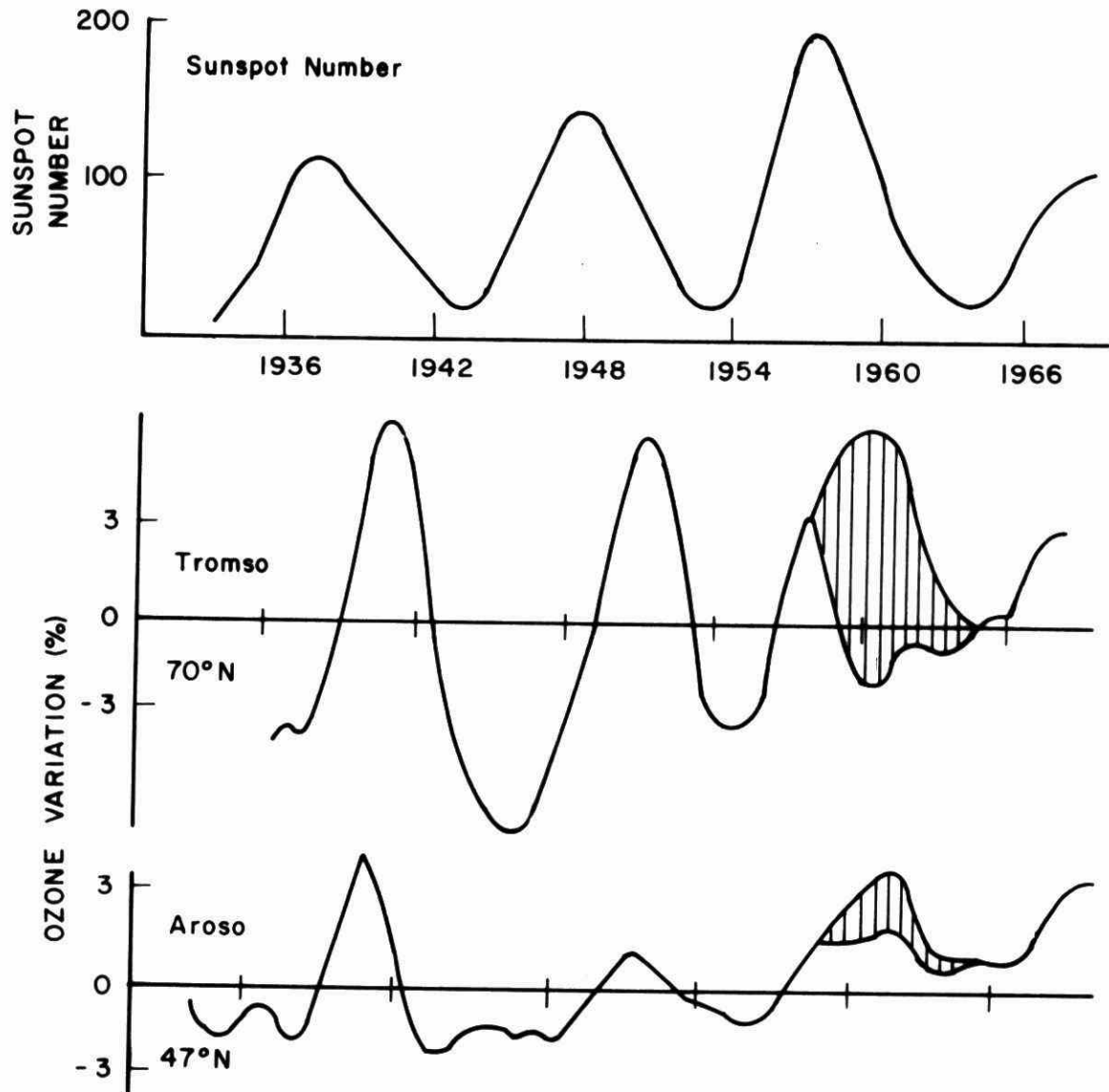


Figure 22: Correlation of O_3 Concentrations With The Sunspot Cycle⁶⁷

which would be expected to have injected large quantities of NO_x, formed in the nuclear fireballs, into the stratosphere. Total ozone levels in the northern hemisphere seem to have increased by about 5 to 10 percent from 1955 to 1970. Since then levels have declined by approximately 1 to 2 percent.

Depletion of ozone levels attributable to the release of FCC's could be as high as one percent up to the present time. However, because of natural variability in ozone levels such a change cannot be identified with any statistical reliability. It is estimated that a change of 5 to 10 percent resulting from anthropogenic activity, persisting and measured for five years, would be required in order to be identified.

It should be stressed that although it may be very difficult to detect human induced reductions in stratospheric ozone levels, which may be small compared to natural variations, they may be of considerable significance because they result in an increase in the long term, net UV-B penetration to the surface of the earth.

14. Expected Effects from Reduction in Stratospheric Ozone Levels

Reducing the amount of ozone in the stratosphere would increase the amount of UV-B radiation (280-320 nm) reaching the earth. It is generally believed that this would cause harmful environmental effects. A variety of possible biological, agricultural, and climatic effects have been

68,69
postulated.

There is persuasive, although not absolutely conclusive, evidence of a direct correlation between solar radiation in the UV-B region and the generally non-fatal (non melanoma, one percent fatality rate) skin cancers in humans. There is also some evidence, although much less conclusive, to support a correlation between UV-B radiation and melanoma skin cancer which is a considerably less prevalent but more frequently fatal form of the disease.

From the relationship between UV-B radiation reaching the earth and the incidence of non-melanoma skin cancers, and UV-B radiation reaching the earth and ozone concentrations in the stratosphere, a one percent reduction in average ozone concentrations will lead to about a 2 percent increase in non-melanoma skin cancer. The National Cancer Institute estimates current incidence of non-melanoma skin cancer in the U.S. to be about 300,000 cases per year.

Further expected health effects could include increased incidence of sunburning, the earlier onset of skin aging, possible eye damage, and excessive synthesis of vitamin D in the skin.

Other possible environmental effects include changes in the physiological, biochemical, anatomical and growth characteristics of some plants, disturbances in aquatic and terrestrial ecosystems, changes in insect behaviour, effects on agricultural chemicals, increased incidence of cancer in livestock, and effects on crop yields as a result of climatic changes or influences on crop disease organisms.

Climatic effects such as changes in temperature, and wind patterns and precipitation are also possible. In a recent publication⁷⁰ it has been suggested that trapping of outgoing infrared radiation by FCC's in the troposphere could cause an increase in the Earth's temperature.

It has also been suggested that some effects⁷¹ could be beneficial to the environment. These include increased vitamin D production in humans, increases in crop yields resulting from modified weather patterns and the effects of increased UV radiation on fungus diseases of cereal crops, and certain modifications to insect behavioral patterns. However, the potential for serious adverse effects is large and the present understanding of the problem does not permit quantitative or qualitative prediction of net changes that could result from a drop in ozone levels in the stratosphere.

15. Current Investigative Programs

a) Study Groups and Task Forces

Since model predictions of ozone depletion resulting from FCC's were announced many groups have been studying the scientific and socio-economic ramifications of the questions raised.

The U.S. federal interagency task forces on Inadvertent Modification of the Stratosphere (IMOS) was formed by the Council on Environmental Quality (CEQ) and the Federal Council of Science and Technology (FCST). After five months

of study this task force produced a report in June 1975 in which it was recommended that "unless new scientific evidence is found to remove the cause of concern, it would seem necessary to restrict uses of fluorocarbons 11 and 12 to replacement of fluids in existing refrigeration and air-conditioning equipment and to closed recycled systems or other uses not involving release into the atmosphere".

The U.S. National Academy of Sciences (NAS) and National Academy of Engineering (NAE) are conducting studies into the man-made impacts on the atmosphere through the Climatic Impact Assessment Program (CIAP). A panel on Atmospheric Chemistry (PAC) was convened to study the FCC question and is expected to report by next year.

The IMOS task force recommended that, if the PAC report confirms the IMOS assessment, then "Federal regulatory agencies (should) initiate rulemaking procedures for implementing regulations to restrict fluorocarbons uses. Such restrictions could reasonably be effective by January 1978..."

In a preliminary report PAC recommended laboratory and atmospheric studies be undertaken in order to aid in assessing the extent to which FCC's pose a threat to ozone levels in the stratosphere. The report also notes that if we wait until a reduction in ozone is directly measured, and attributed to FCC release to the atmosphere, then it could be too late to avoid potential long term drastic effects.

The PAC report recommended that further research be carried out in the following areas:

Atmospheric measurements and modeling:

- direct measurements of the altitude profiles of the following should be carried out - Cl, ClO, OH, HCl, HF, NO, F-11, F-12, CCl₄, CH₃Cl
- determine the effect of latitude and season on the above species concentration profiles
- measure global distribution of trace gases having chemical sinks in the 20 to 50 km regions
- develop better atmospheric models

Reaction rate constants:

- measure reaction rate constants and temperature dependences for the following reactions - ClO with NO, ClO with O, Cl with HO₂, Cl with CH₄, OH with CHFCl₂, OH with CHF₂Cl, and OH with CH₃Cl
- obtain kinetic data for all important reactions of Br

Photolysis:

- measure the solar flux and scattering parameters for the stratosphere
- measure photolysis parameters for the FCC's and ClO

Sources and Sinks:

- sample atmosphere and attempt to identify any other natural or anthropogenic sources of halogen compounds
- obtain data on release of natural and anthropogenic chlorine species to the atmosphere

- measure total chlorine in the atmosphere and compare with release figures
- measure abundance of FCC decomposition products such as COF_2 , COCl_2 , and COFCl
- look for other possible sinks for FCC's
- examine source of chlorine-containing stratospheric particles.

b) Research Programs

A large number of government agencies, university workers, and industrially supported research programs have been launched since the ozone depletion theory was first presented by Rowland and Molina⁵³ in June 1974.

In Canada, the Atmospheric Environment Service of Environment Canada has sponsored several balloon launchings directed toward measuring various chemical species in the stratosphere. Also participating in these flights were Professor H. Schiff (York University) and workers at the National Oceanic and Atmospheric Administration (NOAA). Professor R. Nicholls (York University) is carrying out high resolution spectroscopic studies of sky light in an attempt to measure stratospheric ClO from ground based instruments. Professor Sandorfy (University of Montreal) is carrying out laboratory spectroscopic studies on various chlorine containing compounds.

During the summer of 1975 the Air Resources Branch of the Ontario Ministry of the Environment initiated a study under the "Experience '75" program, to sample and analyse ambient air in the Toronto area.

The purposes were to attempt to quantify the FCC input rate to the atmosphere from the City of Toronto, to

investigate the suitability of using FCC's as air mass tracers and to establish base levels of FCC's in Ontario against which future work can be compared. Further studies are being planned.

In the U.S., government research is being carried out by the Department of Transport (DOT), National Oceanic and Atmospheric Administration (NOAA), National Bureau of Standards (NBS), Department of Defense (DOD), Environmental Protection Agency (EPA), Energy Resource and Development Agency (ERDA), National Aeronautics and Space Administration (NASA), and the National Science Foundation (NSF). In addition, numerous university workers and the National Center for Atmospheric Research (NCAR) - which is supported by a consortium of 14 universities - are working on research projects related to the FCC question.

The main research projects being carried out or proposed by the above agencies are outlined below.

DOT:

- funded the recently completed three-year CIAP program
- supporting chemical kinetic studies at various universities such as Professor F. Kaufman (University of Pittsburgh) and Professor D. Davis (University of Maryland)

NOAA:

- monitoring total ozone in atmosphere
- collecting atmospheric samples at different altitudes and analysing for F-11, F-12, N₂O and CCl₄

- supporting climatic modeling at the Geophysical Fluid Dynamics Laboratory in Princeton

NBS:

- studying some chemical reactions
- collecting and evaluating reaction rate data

DOD:

- atmospheric modeling
- rocket and balloon measurements of solar flux
- balloon sampling of rain and ocean sampling for FCC's
- instrumentation development
- study of some chemical processes

EPA:

- photo-oxidation studies in simulated stratospheric environments with attempts to identify intermediate reaction products
- studies of transport properties of FCC's

ERDA:

- using aircraft and balloons to measure FCC's, CCl_4 , SF_6 , HCl , Cl and Br
- supporting studies by Professor Rowland and Dr. Molina (University of California-Irvine) on stratospheric problems associated with F-22 and other FCC's

NASA:

- supporting programs to measure trace constituents in the stratosphere and troposphere, for example:

- o Professor James Anderson and Dr. Donald Stedman (University of Michigan) are using resonance fluorescence to measure O, OH, Cl, ClO, and Cl
- o Professor Doug Davis (University of Maryland) is using laser induced fluorescence to measure OH, NO₂, and SO₂
- o Dr. Robert Stokes (Battelle-Washington) proposes the use of a radio telescope to look for ClO
- o Dr. Alan Lazrus (NCAR-Boulder) is using filters to trap HCl and to measure ClO
- o Professor R. Nicholls (York University) is carrying out laboratory spectroscopic studies of ClO and ground based measurements of stratospheric ClO using a UV spectrometer
- supporting chemical kinetic studies, for example:
 - o Professor Fred Kaufman (University of Pittsburg)
 - o Professor Doug Davis (University of Maryland)
- continuing with global atmospheric sampling program to collect and analyse air samples for FCC's
- supporting modeling efforts such as a three dimensional model developed by Dr. Ronald Prinn (MIT)

NSF:

- continuing normal research efforts in atmospheric sciences such as:
 - o supporting NCAR
 - o wind measurements in the upper stratosphere (University of Alaska and Georgia Tech)
 - o atmospheric reactions of NO₃ (Colorado State University)

- o atmospheric physics and dynamics (Harvard University)
 - o high altitude chemistry (MIT)
 - o spectroscopic studies of OH, H₂O, HO₂ (University of Michigan)
 - o chemical reactions in the stratosphere (Pennsylvania State University)
- observation of ClO, NO, NO₂, HNO₃, HO₂, and O₃ by the use of a radio telescope is being attempted by Dr. Edward Tilley (Harvard University)

Nineteen manufacturing companies of FCC's (six in the U.S. and thirteen outside the U.S.) are sponsoring research programs through the Manufacturing Chemists Association. By the end of 1975 the group will have committed \$1 - 1.2 million and by the end of 1977 this should rise to a total of \$3 - 5 million.

Areas of sponsored research include monitoring halogen compounds in the troposphere and the stratosphere, balloon borne infrared spectroscopy of FCC's, other halogen compounds, and expected end products, microwave absorption spectroscopy of the ClO radical, exploration of the chemical behaviour of Cl and O compounds by stratospheric simulation, development of an instrument that will measure total Cl and ClO in the stratosphere, reaction rate measurements, sensitivity analysis of models, and one-two- and three-dimensional modeling.

16. Recent Developments and Controversies

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When Rowland and Molina first published their

prediction that the stratosphere could act as a sink for F-11 and F-12 with a subsequent depletion of ozone concentrations, no measurements of any chlorine species in the stratosphere had been reported. Lovelock^{1,2} in 1971 reported measurements of F-11 in clean background air. Within the next three years at least four sets of measurements for F-11^{3,4,5,6} and two for F-12^{5,6} were reported.

The published theory of Rowland and Molina has sparked considerable research efforts by governments, university workers, and industry. As a result several scientific objections to Rowland and Molina's theory have been put forward. These are summarized below and evaluated in the light of best current knowledge.

Arguments have recently been presented in a publication by the Council on Atmospheric Sciences (CAS) entitled "Scientific Evidence Against the Fluorocarbon/Ozone Depletion Hypothesis". The arguments may be summarized as:

- 1) Changes in some of the critical rate constants have lead to a 300 percent reduction in model predictions of ozone depletion.
- 2) The dependence of photolysis rate with temperature for FCC's will lead to a reduced rate of FCC destruction.
- 3) Other halogen containing compounds such as CCl_4 and CH_3Cl have been found in significant quantities in the troposphere. The current input of ClX to the stratosphere from these sources is larger than from all FCC's.

- 4) There are other significant FCC sinks not considered in the original calculations such as ion-molecule reactions, trapping in polar snow, reaction with O('D), and heterogeneous sinks by absorption on aerosols.
- 5) Present understanding of O₃ balancing processes is not complete. For example Br could be much more important for O₃ balance than Cl and a recent report indicates the possibility of large amounts of NO formed in lightning storms could exceed the amount of N₂O presently formed as a result of microbiological activity.

The following comments are presented with respect to these points:

- 1) Some of the critical reaction rates have been revised in the light of recent studies. They are:

- a) Cl + O₃ is now a factor of two slower than^{72, 73} originally thought.
- b) Cl + CH₄ is now 50 percent faster than originally^{72, 73} thought.
- c) OH + HCl is now faster than originally thought.⁶⁴

The changes in model predictions resulting from (a) and (b) above could reduce calculated ozone depletion by a factor of three. However, if (c) is included, as well as recent⁷⁴ measurements of OH profiles in the stratosphere, the net²³ result is a change in the original theory of about 10 percent.

- 2) Preliminary measurements of the temperature dependence of absorption coefficient for FCC's at only one wavelength of

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stratospheric importance showed a decrease in the rate of
photolysis by a factor of two between room temperature and
mid-stratospheric temperatures. However, more recent results²³
over the entire relevant wavelength region indicates less than
a 10 percent temperature effect.

3) Two other halogen species have been found in relatively
large concentrations in the troposphere - CCl_4 ^{4,25,30,3} and^{74,75}
 CH_3Cl .

The commercial use of CCl_4 involving release to the
atmosphere has decreased considerably over the past several
years. The present atmospheric levels may be considered as
steady state (if natural sources) have been dominant in the
past) or on a decline (if anthropogenic sources have signi-
ficantly contributed to present levels). In either case, calcu-
lations show²³ that injection of ClX species (resulting from
photodecomposition of CCl_4) to the stratosphere will not signi-
ficantly affect ozone levels.

CH_3Cl is not in large commercial use resulting in
loss to the atmosphere. Therefore, the relatively large con-
centrations of from 500 to 2000 ppt are likely natural in
origin and hence can be considered to be in a steady state.

CH_3Cl decomposes in the stratosphere as a result of
attack by OH or O('D) and not photolysis. However, the result-
ing vertical stratospheric ClX injection profile resulting
from chemical decomposition is similar to that for the FCC's.
It has been estimated that a steady tropospheric concentra-
tion of from 6,000 to 10,000 ppt is needed before CH_3Cl could
play a significant role in ozone concentration control in²³
the stratosphere.

On the basis of a lifetime of one year for CH_3Cl ,

it has been calculated that in order to maintain the observed steady state concentrations of CH_3Cl its ground level source strength must be considerably larger than that presently for the FCC's. However, ground emission rates alone should not be compared. The injection rate to the stratosphere depends on tropospheric lifetimes as well and this lifetime is much shorter for CH_3Cl than for the FCC's.

4) Other sinks have been considered.

a) Calculations using known rate constants and atmospheric abundances have indicated that ion-molecule reactions are unlikely to play a significant role in FCC chemistry in the atmosphere.

b) Rasmussen³³ has found FCC's concentrated in Antarctic snow at levels from 5 to 20 times that for ambient air. However, it has been²³ estimated that even at these levels polar sinks are smaller than the oceans which cannot account for more than a one percent sink.

c) FCC's react with $\text{O}('D)$ on almost every collision. However, except at very high altitudes, the concentration of $\text{O}('D)$ is very low and reaction of FCC's with $\text{O}('D)$ does not compete with photodissociation as a sink above 15 Km. Below 15 Km the rates of reaction $\text{O}('D)$ with F-11 or F-12 and photolysis are competitive but both are negligible compared

to the rate of vertical transport.

- d) Analysis of stratospheric aerosols ⁴² indicates an insufficient Cl content to account for a major sink by aerosol removal.

5) Although the stratospheric processes and chemistry are not fully understood, present models account for about 80 percent of ozone destroying mechanisms through the Chapman mechanism, NO_x chains (where the major input is N_2O injection from the troposphere formed as a result of microbiological activity) and HO_x chains. This must be considered good agreement in view of the assumptions used.

Bromine could potentially be much more of a hazard in the stratosphere than Cl since it is likely it would be more efficient in entering ozone destroying chain reactions than Cl. ⁷⁸ However, the tropospheric lifetime of Br compounds is probably much shorter than for F-11 or F-12. No significant concentrations of Br containing species has been reported in the troposphere.

17. Conclusion

Since Rowland and Molina first published their theory in June, 1974, numerous university, industry and government groups have launched intensive research programs to further define the magnitude of potential problems following release of FCC's to the environment. Up to the present time, it is reasonable to conclude that no successful challenge to Rowland and Molina's theory has yet been found. However, it

is generally believed, although not unanimously, amongst scientists that even if the ozone depletion theories are correct there would be very little additional harm to the environment if controlling action were to be delayed for about two years. During this time further research can be carried out.

Concern over the use of FCC's has centered around F-11 and F-12 which make up the bulk of FCC usage. However, F-22 is also used in significant amounts (mainly as a refrigerant fluid) and since it contains one H atom it can react^{76,77} with OH in the troposphere.

This tropospheric sink for F-22 is not available to F-11 or F-12 and hence the potential hazard of F-22 release is correspondingly less. For this reason an increased usage of F-22 (when possible) over F-11 or F-12 could be desirable.

Ontario's contribution to the world budget of FCC's is about one percent. Because of the global nature of this question it is clear that if controls decided upon are to be effective, then agreement on an international scale must be reached.

18. BIBLIOGRAPHY

1. J.E. Lovelock, *Nature*, 230, 379 (1971)
2. J.E. Lovelock, *Atmos. Environ.*, 6, 917 (1972)
3. J.E. Lovelock, R.J. Maggs, R.J. Wade, *Nature*, 241, 194 (1973)
4. P.E. Wilkniss, R.A. Lamontagne, R.E. Larson, J.W. Swinnerton, C.R. Dickson, T. Thompson, *Nature, Phys. Sci.*, 245, 45 (1973)
5. C.W. Su, E.D. Goldberg, *Nature*, 245, 27 (1973)
6. N.E. Hester, E.R. Stephens, O.C. Taylor, *J. Air Pollut. Control Ass.*, 24, 591 (1974)
7. F.S. Rowland, M.J. Molina, *Rev. Geophys. and Space Phys.*, 13, 1 (1975)
8. L. Peterson, *Can. Consumer*, 5, 21, Oct. 1975.
9. P. Brodeur, *The New Yorker*, 47, April 7, 1975
10. "The Science and Technology of Aerosol Packaging", Edited by J.J. Sciarna and L. Stoller, John Wiley (1974)
11. R.L. McCarthy, Paper presented at the American Geophysical Union meeting, San Francisco, Calif. Dec., 1974
12. "Synthetic Organic Chemicals: U.S. Production and Sales (1972)", U.S. Tariff Commission Publication 681, Government Printing Office, Washington, D.C., 1974
13. *Chemical Marketing Reporter*, August 21, 1972
14. *Chemical Marketing Reporter*, January 1, 1973
15. *Chemical Marketing Reporter*, May 13, 1974
16. Technical Presentation by the Technical Committee on Environmental Aspects of Chlorofluorocarbons-Ottawa, D. Samson, June 1975
17. *Chemical Week*, 14, June 11, 1975
18. P.H. Howard, A. Hanchett, *Science*, 188, 217 (1975)
19. American Society of Heating, Refrigeration, and Air Conditioning Engineers Handbook- New York 1973, "Engineered Refrigeration Systems (industrial and commercial)"
20. I.C.T. Nisbitt, A.F. Sarofim, *Environ. Health Perspect.*, 1, 21 (1972)

21. "Plastic Foams"-part 2, p. 459, J.K. Barker, P.G. Gemeinhardt, Edited by K.C. Frisch and J.H. Saunders, Dekker, New York, 1973
22. R.T. Darby and A.M. Kaplan, Appl. Microbiol., 16, 900 (1968)
23. F.S. Rowland, private communication
24. DuPont Management Bulletin, 4, Feb. 1975
25. P.E. Wilkniss, J.W. Swinnerton, D.J. Bressan, R.A. Lamontagne, R.E. Larson, J. Atmos. Sci., 32, 158 (1975)
26. P.E. Wilkniss, J.W. Swinnerton, R.A. Lamontagne, D.J. Bressan, Science, 187, 832 (1974)
27. J.E. Lovelock, S.A. Penkett, Nature, 249, 434 (1974)
28. R.A. Cox, A.E.J. Eggleton, R.G. Derwent, J.E. Lovelock, D.H. Peck, Nature, 255, 118 (1975)
29. N.E. Hester, E.R. Stephens, O.C. Taylor, Environ. Sci. Technol., 9, 875 (1975)
30. J.E. Lovelock, Nature, 252, 292 (1974)
31. L.E. Heidt, R. Lueb, W. Pollock, D.H. Ehhalt, Submitted to J. Geophys. Res. Lett. (1975)
32. A.L. Schmeltekopf, P.D. Goldan, W.R. Henderson, W.J. Harrop, T.I. Thompson, F.C. Fehsenfeld, H.I. Schiff, P.J. Crutzen, I.S.A. Isakson, E.E. Ferguson, Submitted to J. Geophys. Res. Lett. (1975)
33. R.A. Rasmussen, Unpublished results
34. "Chemistry of Organic Fluorine Compounds", M. Hudlicky, McMillan Co., New York, 1962
35. "The Aerosol Handbook", M.A. Johnsen, W.E. Dorland, E.K. Dorland, W.E. Dorland Co., Caldwell, N.J., 1972
36. P.A. Saunders, Soap Chem. Specialties, 36, 95 (1960)
37. J.D. Monford, J. Soc. Cosmet. Chem., 15, 311 (1964)
38. S. Bohac, J. Soc. Cosmet. Chem., 19, 149 (1968)
39. H.L. Sandoval, R. Atkinson, J.N. Pitts, J. Photochem., 3, 325 (1974/75)
40. "Mesospheric Models", V. Mohnen, NBSIR-74-430, January 1974
41. D.J. Hoffman, Can. J. Chem., 52, 1519 (1974)

42. "Climatic Impact Assessment Program, Survey Conference,"
February 15-16, 1972, DOT-TSC-OST-72-13
43. C.R. Zobel, A.B.F. Duncan, J. Amer. Chem. Soc., 77, 2611
(1955)
44. J. Doucet, P. Sauvageau, C. Sandorfy, J. Chem. Phys. 58,
3708 (1973)
45. M. Ackerman, "Mesospheric Models", Dordrecht, Netherlands,
1971
46. P.J. Ausloos, Unpublished results
47. J.R. Major, J.P. Simons, Adv. Photochem., 2, 137 (1964)
48. R. Milstein, F.S. Rowland, J. Phys. Chem., 79, 669 (1975)
49. D. Marsh, J. Heicklen, J. Phys. Chem., 69, 4410 (1965)
50. S. Chapman, Mem. R. Meteorol. Soc., 3, 103 (1930)
51. J.C. McConnell, M.B. McElroy, J. Atmos. Sci., 30, 1465
(1973)
52. M. Nicolet, Can. J. Chem., 52, 1381 (1974)
53. M.J. Molina, F.S. Rowland, Nature, 249, 810 (1974)
54. M.J. Molina, F.S. Rowland, Geophys. Res. Lett., 1 309 (1974)
55. F.S. Rowland, New Sci., 717 (1974)
56. M.J. Molina, F.S. Rowland, J. Phys. Chem., 79, 667 (1975)
57. P.J. Crutzen, Geophys. Res. Lett., 1, 205 (1974)
58. R.J. Cicerone, D.H. Stedman, R.S. Stolarski, Geophys. Res.
Lett., 2, 219 (1974)
59. R.J. Cicerone, R.S. Stolarski, S. Walters, Science, 185,
1165 (1974)
60. S.C. Wofsy, M.B. McElroy, N.D. Sze, Science, 187, 535 (1975)
61. S.C. Wofsy, M.B. McElroy, Can. J. Chem., 52, 1582 (1974)
62. P. Crutzen, Can. J. Chem., 52, 1582 (1974)
63. R.S. Stolarski, R.J. Cicerone, Can. J. Chem., 52, 1610 (1974)
64. M.S. Zahnison, F. Kaufman, J.G. Anderson, Chem. Phy. Lett.,
27, 507 (1974)
65. M.B. McElroy, S.C. Wofsy, J.E. Penner, J.C. McConnell, J.
Atmos. Sci., 31, 287 (1974)

66. R.K.R. Vupputuri, Atmospheric Environment Service, Environment Canada Report, 1975
67. H.S. Johnston, Acta Astonautica, 1, 135 (1974)
68. "Environmental Impact of Stratospheric Flight - Biological and Climatic Effects of Aircraft Emissions in the Stratosphere", National Academy of Sciences Publication, 1975
69. "Fluorocarbons and the Environment", Report of U.S. Federal Task Force on Inadvertent Modification of the Stratosphere, June 1975
70. V. Ramanathan, Science, 190, 50 (1975)
71. J.F. Leach, Private communication
72. D. Davis, R. Watson, Unpublished results
73. F. Kaufman, J. Anderson, Unpublished results
74. J. Anderson, Unpublished results
75. J.E. Lovelock, Unpublished results
76. C.J. Howard, K.M. Evenson, Submitted to J. Chem. Phys. (1975)
77. R. Atkinson, D.A. Hansen, J.N. Pitts, Jr., J. Chem. Phys. (In Press-1975)
78. S.C. Wofsy, M. McElroy, Y.L. Yung, Geophys. Res. Lett., 2, 215 (1975)
79. J. Pitts, Unpublished results
80. G.B. Lubkin, Physics Today, 34, October (1975)
81. P. Cutchis, Science 184, 13 (1974)